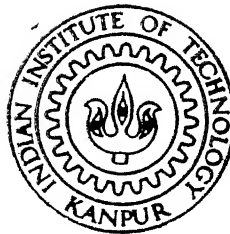


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# IMPROVEMENT IN IMPACT INDUCED DAMAGED AREA IN FRP LAMINATES

by  
RAMAYAN PRASAD GUPTA



DEPARTMENT OF MECHANICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

August, 1996

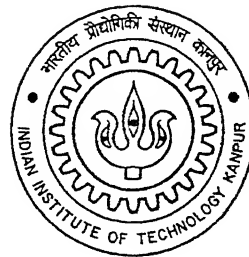
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# **IMPROVEMENT IN IMPACT INDUCED DAMAGED AREA IN FRP LAMINATES**

A Thesis Submitted  
in Partial Fulfilment of the Requirements  
for the Degree of  
**MASTER OF TECHNOLOGY**

by  
**RAMAYAN PRASAD GUPTA**



to the  
**DEPARTMENT OF MECHANICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY  
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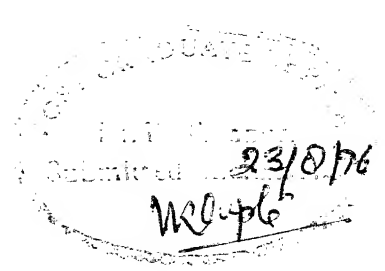
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# CERTIFICATE



It is certified that the work contained in the thesis entitled "**IMPROVEMENT IN IMPACT INDUCED DAMAGED AREA IN FRP LAMINATES**" by **RAMAYAN PRASAD GUPTA**, has been carried out under our supervision and that this work has not been submitted elsewhere for a degree.

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Kanpur

AUGUST, 1996



Dedicated to

**MY PARENTS**

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RAMAYAN PRASAD GUPTA

## *ABSTRACT*

A study has been carried out to improve the impact damage area tolerance of Glass fibres/Epoxy composite laminates (FRP). The poor impact resistance of composite laminate is mainly due to brittle nature of both reinforcing material (Glass or carbon fibres) and matrix material. Thus by reducing the brittleness of matrix material, the impact resistance can be increase considerably.

In the present study two kinds of glass fibre reinforced plastic laminates are prepared (i) with unmodified Epoxy resin and (ii) with Epoxy resin modified with CTBN and triphenylephosphine in inert atmosphere of Nitrogen gas. The specimens prepared from these laminates are investigated to find how impact resistance, inter laminar fracture toughness and tensile properties change with the modification of epoxy.

The impact test has been carried out by impacting a FRP panel with a projectile which is accelerated in an air gun. The projectile weighs 11.8 gm and its nose is hemispherical. The impact tests were made with projectile velocity ranging between 35 and 110 m/s. The impact damage area of modified epoxy laminate was found 40% less than the damage area of the unmodified epoxy laminates in the entire velocity range.

The interlaminar fracture resistance in mode I is determined with DCB specimen. The average value of interlaminar critical energy release rate ( $G_{Ic}$ ) for unmodified laminates

was found to be  $339 \text{ J/m}^2$  which was increased to  $477 \text{ J/m}^2$  for modified laminates.

The mode II interlaminar fracture toughness has been determined with the help of End Notched Flexural(ENF) specimen. The average  $G_{IIc}$  obtained in experiments was  $923 \text{ J/m}^2$  for unmodified laminate specimens; it increased to  $1359 \text{ J/m}^2$  for modified laminate specimens.

To investigate the effect of matrix modification on tensile properties of the laminates, the specimens are tested in an Instron testing Machine. The tensile experiments showed that modification of epoxy does not appreciably change the modulus and tensile strength of laminates. The modulus of unmodified laminate was found to be  $20 \text{ GPa}$  as against  $18.5 \text{ GPa}$  for modified laminate. The tensile strength increased slightly with modification from  $286$  to  $317 \text{ MPa}$ .

The SEM micrographs of impacted laminates were studied to investigate the mechanisms responsible for damage area improvement. The plastic deformation of matrix and crack tip bridging by rubber particles is believed to be mainly responsible for better impact damage area performance of modified laminates over unmodified laminates.

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# CHAPTER 1

## INTRODUCTION

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### 1.1 INTRODUCTION

Rapid technological development makes demands for materials which can withstand the severe working and loading conditions, particularly in the field of air and ground transportation, structures, space ships, and sport goods. These applications require demand of materials of light weight, high strength, high toughness, and environment and corrosion resistance. With demand for such versatile properties, single materials (aluminium, steel etc.) are slowly losing ground and hence the expectation for composite materials has arisen.

Polymer composites consist of two or more phases, all phases are chemically and physically different. These materials have one or more discontinuous phases (fibres) embedded in continuous phase (matrix). The discontinuous phase is generally stronger and stiffer than continuous phase.

Polymer composites are known for their distinct properties such as high specific modulus

and specific strength, fatigue resistance and corrosion resistance. But these properties depend on the properties of constituents as well as on the behaviour of interface between the fibres and matrix. Though composites have many attractive properties but their impact induced resistance is poor.

The most of matrix materials used(i.e.epoxy) are inherently brittle in nature. Due to incompatibility of resin and fibres, the interfacial bonds are also not strong. Moreover, in a laminate there is no reinforcement of fibre along the thickness and there is a matrix rich zone having inherently very little energy absorbing capacity at the interface. It makes them vulnerable to interply or delamination failure under impact loading. Thus the various factors that contribute to delamination of polymer composites are complex nature of induced stresses, brittle nature of constitutes, poor interface bonds, difference in properties of constituent elements like modulus, complex energy absorbing mechanism, microcracks, and material discontinuity etc. Due to absence of any crack arresting medium, once a delamination crack is initiated by an impact it propagates at very high speed. As a result even a minute impact load like hailstorm, runaway debris, drop of work tools, foreign objects impacts(bird hitting) etc. causes extensive delamination around the point of impact. On the other hand when a sheet of conventional metals is impacted by a foreign body usually is not cracked because of local yielding. Further the propagation of crack is inhibited owing to work-hardening of metals. Therefore, impact loading causes more severe damage in composite materials as compared to conventional metals.

## **1.2 DELAMINATION - A MAJOR FAILURE MODE**

As result of the laminated nature of most composite structures, two principal transverse directions must be considered, which are perpendicular to one another, namely, the interlaminar and the trans-laminar directions. Correspondingly two different failure modes are considered with fracture propagating either between or across the layers of the laminate. Due to the absence of through the thickness reinforcement, the laminate is prone to interlaminar failure or delamination. The presence and growth of delamination crack results in the progressive reduction of stiffness and strength of composites. These lead to the loss of structural integrity and contribute to the final failure of the structure.

## **1.3 REVIEW OF LITERATURE**

The composite materials under impact loading generally fail due to interlaminar crack formation and subsequently its propagation with high speed. Therefore, there arises a need of some tough materials which can inhibit crack initiation and the propagation between the laminae of a composite laminate. Several ways have so far been suggested (addition of elastomers and thermoplastic to epoxy resin, fiber hybridization, interleaving of tough material and stitching) to improve the impact induced damage tolerances. But the failure of composite laminates under foreign object impact damage is still remains a challenging hurdle in the path of wide spread use of the composite material.

## Rubber toughening of epoxy resins

From last two decades, there have been several attempts to modified impact properties of bulk thermosetting resins by several investigators. But there is not much work done in the arena of improvement of impact properties of fibre composite materials.

Siebert and Rowe (1974) found that toughness and fracture energies of thermosetting resin can be increased by adding both CTBN or preformed rubber particles (latexes of different grades). In their work they found that impact strength for CTBN liquid increases with acrylonitrile content(upto 16%) but impact strength in case of other latexes do not depend upon the acrylonitrile content. They found that impact strength of modified epoxy resin improves five fold over unmodified epoxy.

Manziona and Gillham (1981) have used homogeneous mixer of CTBN and EPON 828 (epoxy resin) for their specimens. They found that fracture toughness depends upon a number of parameters e.g.fibre volume fraction, domain size, particle distribution of phase separated rubber and laminate parameters (curing mechanism, stacking sequence and orientation of lamiane etc.). The character of separated rubber depend upon compatibility, rate of nucleation, domain growth and quenching of morphological developments of gelation. The increase of compatibility between CTBN and epoxy inhibits the phase separation of rubber. The CTBN of higher acrylonitrile content was found to be more compatible with epoxy therefore CTBN of high acronitrile content( more than 20% ) is less effective in toughness enhancement. They found phase separation before gelation of epoxy was effective because in latter stage it form

homogeneous solution. In another study Manzione and Gillham (1981) observed that impact properties of bulk epoxy depend on phase separation of rubber and strain rate loading. At low strain rate single phase rubber solution (no separation of rubber particles) imparts greater impact resistance while at higher strain rate two phase system shows greater resistance for delamination. They also found that presence of phase separated rubber is more detrimental to tensile modulus than presence of dissolved rubber(single phase) in matrix material.

Bascome and Huston (1984) used mixture of epoxy(DGEBA), piperidine(5percent by weight) and CTBN as matrix material to make composite laminates. They used double cantilever beam(DCB) specimen to determined the interlaminar fracture energy mode I. They found that 25 fold increase in matrix interlaminar fracture energy imparts only 4 fold increase in the interlaminar fracture of composite laminates. They also observed that crack tip deformation zone not only restricted between the plies but also travels across the plies. This reduces the restriction imposed by fibres on the crack tip deformation zone. They also found that use of tough matrix material in case of unidirectional composite is not as much beneficial as in case of woven fiber composite.

Dusek et al. (1984) searched a possibility of toughening the bulk epoxy resin by carboxyl terminated and hydroxyl terminated liquid polybutadienes (PBD) in place of conventional CTBN liquids. The main hurdle in this work was that PBD is less compatible with epoxy. This hurdle can be overcome by attaching polar block (e.g. polyester block). The PBD solution phase separated at room temperature but forms a continuous single phase solution at higher temperatures. The impact properties obtained



by this modification were comparable with those obtained by CTBN modification.

Gilwe and Nir (1984) modified epoxy resin with CTBN and brominated epoxy resin. The impact properties of graphite/epoxy laminate were determined by measuring shear strength after falling ball impact and instrumented impact test. For preparing solution, they mixed epoxy (tris epoxy novolac and TGDDM) and CTBN in presence of triphenyl phosphine in nitrogen atmosphere. It was observed that upto 27 percent rubber content, increase in impact properties obtained. The brominated rubber gives better impact properties than CTBN epoxies. The test velocity used were in the range of 2- 3 m/sec. However, toughened laminates were not tested at higher impact velocities of 30-120 m/s.

Kim et al. (1991) has studied the fracture toughness of CFRP both in mode I and transverse impact fracture. They used both rubber modified epoxy and rubber modified epoxy with  $Al_2O_3$  fibres or powder as toughness enhancement medium. The fracture toughness was combined effect of plastic straining of rubber and embrittle behaviour of  $Al_2O_3$ . They observed that addition of  $Al_2O_3$  particles in absence of rubber does not helps in enhancement of fracture resistance rather it deteriorates it. For brittle resin, critical energy release rate ( $G_{Ic}$ ) of composite was higher than  $G_{Ic}$  of matrix, but as the resin  $G_{Ic}$  is increased above 500 J/m<sup>2</sup>, the incremental increase in the composite  $G_{Ic}$  is much smaller than that in the resin  $G_{Ic}$ .

### Coating of fibres

Coating the fibres with a thin layer of rubber or thermoplastic prior to impregnation with

resin offers another possible approach to toughening of composite (Morley et al. 1974). The major limitation of this method is that coating can subsequently dissolve in the resin leading to product of simple resin fibre composites. Moreover, this mixing reduces glass transition temperature of matrix hence strength of composite also deteriorates.

McGarry et al. (1985) coated the fibres(carbon fibres) with CTBN instead of mixing CTBN with matrix material for toughness enhancement of composite. He carried out sizing on fibres with the solution of Epon 828 and CTBN before coating fibres with CTBN. This was done for improving adhesion of rubber with fibres. The presence of rubber coating enhances the damage tolerances. For obtaining desire results good adhesion and proper curing of rubber is necessary.

Atins (1975) has reported improved toughness of boron fibre epoxy composite which was achieved by intermittent coating of fibres. Alternate regions along the fibres of high and low interfacial shear strength produced low and high interfacial toughness respectively. Compared with the uncoated fibres, silicon vacuum grease intermittent coatings gave about 33% increase in toughness whereas polyurethane intermittent coatings provided an increase of about 40%.

Jones et al. (1977) used Dow corning 200 fluid for coating E-glass fibres in order to design strain rate sensitive composites with polyester and polyethylene resins. The reported toughness improvement was about twice the toughness of the uncoated samples. However, as has been reported, these interfaces result in some decrease in tensile strength, thus necessitating a toughness-strength trade-off (Williams and Kousionneois,

1978).

### **Interleaving of tough adhesive materials**

Interleaving of a layer of tough material in between the laminae of laminate is another possible method of toughness modification of composites. The major disadvantage of this system is a weight penalty of laminate. The tough layers of resin have low stiffness and strength of laminate, requiring additional plies in a laminate to maintain design properties. Moreover, tensile and bending strength of interleaved laminates decreases further after an impact with foreign body beyond a velocity range.

Riewald et al.(1970) have studied the impact behaviour of both unhybrid and hybrid composite laminates under instrumented charpy test and three point beam test. They tried to improve the toughness and the fracture resistance of laminate by impregnating Kevlar fibre laminae in between graphite/epoxy laminate. They found Kevlar - graphite/epoxy laminates have higher impact resistance energies.

Ishai et al.(1988) also used concept of tough adhesive(HTS-7) interleaving. But they used interleaving only at high points like flaws, discontinuities, inclusions, holes and free edges. It improves  $G_{Ic}$  upto six fold and  $G_{IIc}$  upto four fold compared with the reference brittle system. Delamination was found to propagate through the adhesive in a cohesive failure mode. Hence the adhesive toughness can be translated to improved composite interlaminar fracture toughness(IFT). This selective interleaving saves weight of composite compared with same toughness enhancement with interlaminar interleaving.

McKenna et al. (1974) tried to improve interlaminar strength by fibre surface treatment, style of reinforcement and matrix material modification. It was found that interlaminar strength can be improved by addition of chopped nylon fibres in between the laminae of a laminates. Interlaminar properties was found better when small volume of nylon fibres stitched along thickness of original laminate before matrix impregnation.

Lea et al. (1980) used the intermittent mylar layer in between the graphite prepreg laminates to enhance fracture toughness of laminates. In their work fracture toughness was increased, while tensile strength drops from 500 MPa to 400 MPa and elastic modulus remain same. The mylar layer of 7 micron thick containing an array of fine holes was used to vary the amount of contact area between plies of tapes.

Chan et al. (1984) used tough adhesive between the laminae the laminate for toughness enhancement. The adhesive in strip form used was FM100 an American Cyanamide product. Delamination arrest depends upon reducing the percentage of the  $G_I$  component in the total strain energy release rate. It was also observed that mixed mode edge delamination was effectively suppressed by placing a layer of tough adhesive material along the edge of laminate.

Kinloch and Huston (1984) proposed a toughening mechanism in which a greater extent of energy dissipation occurs in the in vicinity of crack tip. The large crack tip deformation zone permits blunting of crack tip and this blunting decreases load concentration at tip of crack.

Evans et al.(1985) enhanced the toughness of Graphite/Epoxy by non conventional methods like interleaving of layers of high ductility in discrete manner in between layers of laminae. By this lay-up both structural tolerances and damage tolerances of composite increased. The residual compressive strength after impact of interleaved composites was found to be twice of that observed with panels without interleaves. The interleaving also does reduces cracking under flat-wise impact and preserves edge compressive strength.

Broutman et al. (1971) used glass spheroids between two laminae instead of other shape because of better stress distribution property of the shape. The reinforcement of resin with glass spheroids reduces the crack initiation energy but increases the crack propagation energy. They also observed that when glass spheroids were given surface treatment laminate exhibits better resistance than laminate of unmodified spheroids impregnation.

Chan et al. (1991) has investigated interleaving thin layers of epoxy resin modified with reactive rubber (CTBN) or poly urethane, instead of interleaving adhesive layers between laminas. The  $G_{Ic}$  values composite(Graphite/Epoxy) were only improves 25-50 percentage. This occurs due to fibre breakage and fibre bridging at fracture surface. The  $G_{IIc}$  values of modified composite were found 2-3 times higher. Thus interleave resin appears to be capable of undergoing extensive plastic deformation under shear mode. A good correlation was found between  $G_{Ic}$  of interleave epoxy and interlaminar  $G_{IIc}$  of laminate.

## Stitching

Liue et al.(1990) investigate the effect of stitching on Glass/epoxy, graphite/epoxy and Kevlar/epoxy prepreg laminates. He observed that delamination resistance can be improved by the through the thickness stitching. It was found that through the thickness stitching could reduce the delamination area in composite plates when investigated under low velocity impacts. However, The technique has not becomes popular owing to problems of laminate fabrication.

## Experimental methods

In literature, there are a number of reports concerned with the measurement of mode I interlaminar fracture toughness in composite materials. The double cantilever beam (DCB) type configuration is one of the most common used specimen geometries.

Keary et al.(1985) have used double cantilever beam (DCB) specimen to measure interlaminar fracture toughness in mode I. They analyzed the data through several different schemes(critical energy release rate determination of the J-integral, a compliance calibration procedure and analytical solution based on linear beam theory) and compared them with one another.

Devitt et al.(1980) predicted the mode I delamination resistance of Glass/Epoxy laminates by using spilt beam specimen with mid plane crack and using nonlinear beam analysis. The testing was done in Instron tensile testing machine at ambient environment

and constant displacement mode with cross head speed 2.5 cm/minute.

Carlsson et al. (1986) has used end notched flexure (ENF) specimen for finding mode II fracture toughness. They also analyzed the effect of shear deformation and the influence of friction between the crack surfaces in the fracture toughness determination. The ENF specimen has also been used by Moron et al. (1987) to determine mode II interlaminar fracture toughness for various types of fiber reinforcement.

## **1.4 OUT LINE OF PRESENT WORK**

The present study has been devoted to increase the impact damage area tolerances of Glass/epoxy composite laminates. For this, matrix materials has been modified with carboxyl terminated butadiene acrylonitrile(CTBN) rubber. In chapter 2, the laminates basic raw materials with their properties and laminate preparation with both modified and unmodified epoxy resin have been described. The epoxy is modified with CTBN and triphenylephosphine in the inert atmosphere of Nitrogen gas. The basic curing mechanism of epoxy CTBN and toughening mechanism of epoxy resin by CTBN are also been presented in Chap2.

In the subsequent four chapters, the effect of modification of epoxy on the following laminate characteristics is investigated :

- |   |           |
|---|-----------|
| (i) Impact area damage tolerance              | chapter 3 |
| (ii) Mode I interlaminar fracture toughness   | chapter 4 |
| (iii) mode II interlaminar fracture toughness | chapter 5 |

In the chapter 7, the summary of all the investigations, conclusion drawn and suggestion for future work are discussed.



## **CHAPTER 2**

# **LAMINATE MATERIAL PROPERTIES AND PREPARATION**

---

### **2.1 INTRODUCTION**

In this chapter basic raw materials of laminate preparation with their properties are described. The procedure of laminate preparation and matrix modification is presented. The curing mechanism of basic elastomers and elastomer toughening have been described.

### **2.2 BASIC RAW MATERIALS**

The details of the basic raw materials for laminate preparation are discussed in this section. Chemicals used for laminate toughening are discussed in sec. 2.3.

### 2.2.1 Formulation of Epoxy Resin Mixture

The unmodified epoxy resin mixture has following compositions

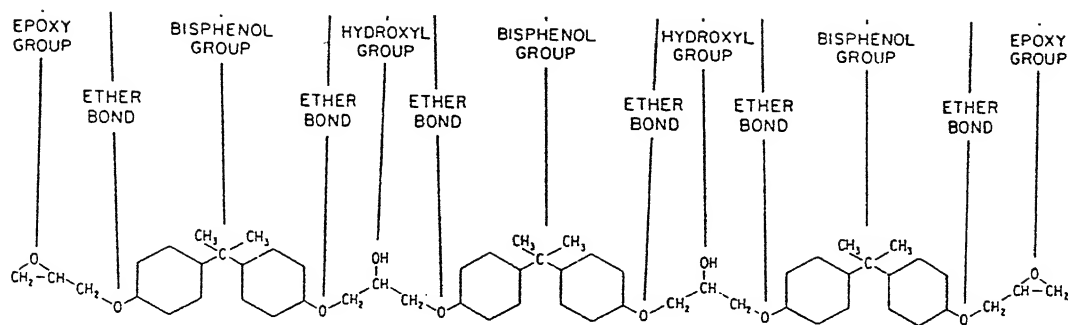
ARALDITE	LY 556	100 Parts by weight
HARDENER	HT 976	35 parts by weight
ACCELERATOR	XY 73/HT 973	1 parts by weight
COUPLING AGENT ( $\gamma$ - Amino propyl triethoxy silane)		0.5 parts by weight

#### Araldite LY 556

This is a liquid unmodified diglycidyl ether of bi-shphenol A (DGEBA) epoxy resin. It is procurred from Hindustan-Ciba Geigy Ltd. Bombay India. Some of its physical properties are:

Viscosity at 25°C	9,000 to 12,000 cP
Epoxy content	5.20 to 1.20 equiv/Kg
Density at 25°C	1.10-1.20 gm/cm <sup>3</sup>
Flash point	> 200°C

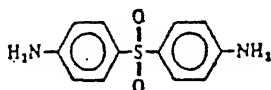
The chemical structure of diglycidyle ether of bishphenol A is



### Hardener HT 976

Hardener is a substance added to basic resin to promote or control curing action by taking part in it. Hardener HT 976 is a 4,4'-Diamino diphenyl sulphone (DDS), an Ciba Geigy product.

It is an aromatic amine defined as one in which the amine nitrogen is attached directly to an aromatic ring as shown below :

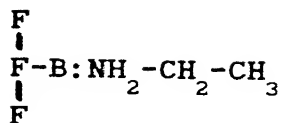


Aromatic amines are generally solids at room temperature. They are converted into liquid form by various techniques such as melting, Eutectic blending, adduct formation and modifying diluents.

### Accelerator XY 73 / HT 973

Accelerator is a substance which is added to mixture of resin and hardener to speed up the curing reaction. HT 973 is Boron trifluoride Mono ethylene amine ( $\text{BF}_3\text{-MEA}$ ) with

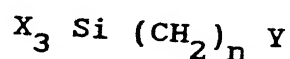
chemical structure :



With the glycidyl ether resins(DGEBA), the reaction of HT 976 (DDS) is sluggish, therefore phenols and borons trifluoride complexes are normally used. However, XY73 should not be used as lone curing agent because it results in brittle matrix.

### Silane Coupling

The chemical treatments applied during the forming of glass-fibres are called sizes. There are of two types sizes, Temporary sizes and compatible sizes. The temporary sizes are applied to minimize degradation of strength resulting from abrasion of fibres to one another. The compatible sizes are applied to improve initial adhesion of resin to glass and to reduce environment forces on this bond. The compatible sizes are called coupling agents such as organofunctional silane. They have chemical formula as follows :

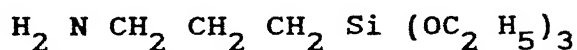


where  $n = 0 - 3$

Y = organofunctional group that is compatible with polymer matrix

x = Hydrolyzable group, on silicon

$\gamma$  - Amino propyl triethoxy silane has the following structure



The manufacturers of fibres apply compatible sizes to glass fibres from 0.1 to 0.5 percentage of the glass. However, to counter for any discrepancies in their application during fibre manufacturing, it has been recommended to add 0.5 % of silane coupling to epoxy resin.

### 2.2.2. Fibres

In the present work unidirectional glass fibres are used as a reinforcement material. These fibres have been procured from Fother Gill Engineered Fabric Ltd England. The density of unidirectional fibre is 500 gm/m<sup>2</sup>. The fabric is made from 1200 tex roving and 40 roving per centimetre.

## 2.3 Formulation of Rubber Modified Epoxy Resin

The modified epoxy resin has following compositions

Araldite	LY 556	100 Parts by weight
Hardener	HT 976	35 parts by weight
Accelerator	XY 73/HT 973	1 parts by weight(in solid state)
Silane		0.5 parts by weight
CTBN 1300X8		15 PARTS BY WEIGHT
Triphenylphosphine		0.15 Parts by weight

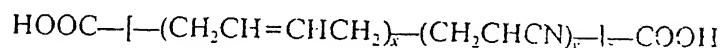
### Carboxyl Terminated Butadiene Acrylonitrile Rubbers(CTBN)

The CTBN's are low molecular reactive rubbers. It is reported by Manzoine et al. that among various grades of CTBN's, CTBN 1300X8 gives optimum property improvement. The present work also uses CTBN 1300X8 for toughening of laminate.

These polymers are available in various grades according to their acrylonitrile content, generally varies from 0 to 27 % . Their average molecular weight varies from 3400 to 4000 and solubility parameter from 8.04 to 9.14. These rubbers have carboxylic group

( $\begin{array}{c} \text{O} \\ || \\ -\text{R}-\text{C}-\text{OH} \end{array}$ ) as active site for reaction.

The representative structure is :



where x,y and z have typically values 5, 1 and 10 respectively.

Typical properties of CTBN 1300X8 are acrylonitrile content 18%, carboxyl content acid number 29 and EPHR 0.052, Brookfield viscosity 135000 cP at 27°C, solubility parameter 8.77, specific gravity 0.948 at 25°C, functionality 1.8 and molecular weight 3600.

### **Triphenyl Phosphine**

This is an amine catalyst and used to speed up the reactivity of CTBN and epoxy. Initially CTBN reacts with triphenyl phosphine to form carboxylic salt, which then reacts with epoxy groups to produce epoxy-terminated rubber.

## **2.4 PREPARATION OF MODIFIED EPOXY RESIN**

First 100 parts by weight of epoxy resin and 15 parts of CTBN 1300X8 were placed in a specially designed nitrogen heating chamber. The solution is heated up to 90°C, so that both epoxy and CTBN mix properly; triphenyl phosphine (0.15 parts) is then added to the solution. The solution is stirred at constant temperature for three minutes. The solution is further heated up to 100°C in N<sub>2</sub> atmosphere. The temperature is maintained for 50 minutes. Afterwards, temperature is again raised to 125°C and maintained for 20 minutes. It is worth noting that heating is done strictly in N<sub>2</sub> atmosphere. Finally, solution is heated to 145°C and maintained for 20 minutes. Now the heating element is switched off and solution is allowed to cool to atmosphere temperature.

This prereacted solution is transferred to another pot and heated upto 100°C, Then hardener HT 976 is added into solution. The solution is further heated to 130°C, so that hardener is completely dissolved in prereacted mixture. The solution is cooled down to 60°C and, accelerator XY 73 and silane are mixed.

## 2.5 NITROGEN CHAMBER

This section describes the construction of the nitrogen chamber used for prereaction of CTBN with epoxy resin in inert atmosphere. The body of chamber is made from steel pipe of 100mm diameter which is welded at its bottom with a mild steel plate of 10mm thickness and 110 mm diameter as shown in Fig 2.1. At the height of 65mm from bottom, there is provision for nitrogen gas inlet and outlet through 12.5mm diameter nozzles. The nozzles were tilted at the angle of 60°C with horizontal as shown in Fig. 2.1. The nitrogen gas is released in atmosphere through bubbling in a high viscous oil to avoid back flow of air into chamber.

At the top end of chamber a steel flange of outside diameter 150mm is welded four tapped holes are on PCD of 130mm as shown in Fig. 2.1.

In order to make chamber air tight, a rubber sheet is used between cover plate and the flange of the chamber. The cover plate is made of circular steel plate of 150mm diameter. The four holes are drilled in cover plate at diametral position as shown in Fig. 2.2. In the centre of cover plate, a hole of 13mm diameter is drilled for inserting thermocouple to recording the temperature. Fig.2.3. shows photograph of Nitrogen



chamber assembly used for preparing epoxy/CTBN mixture.

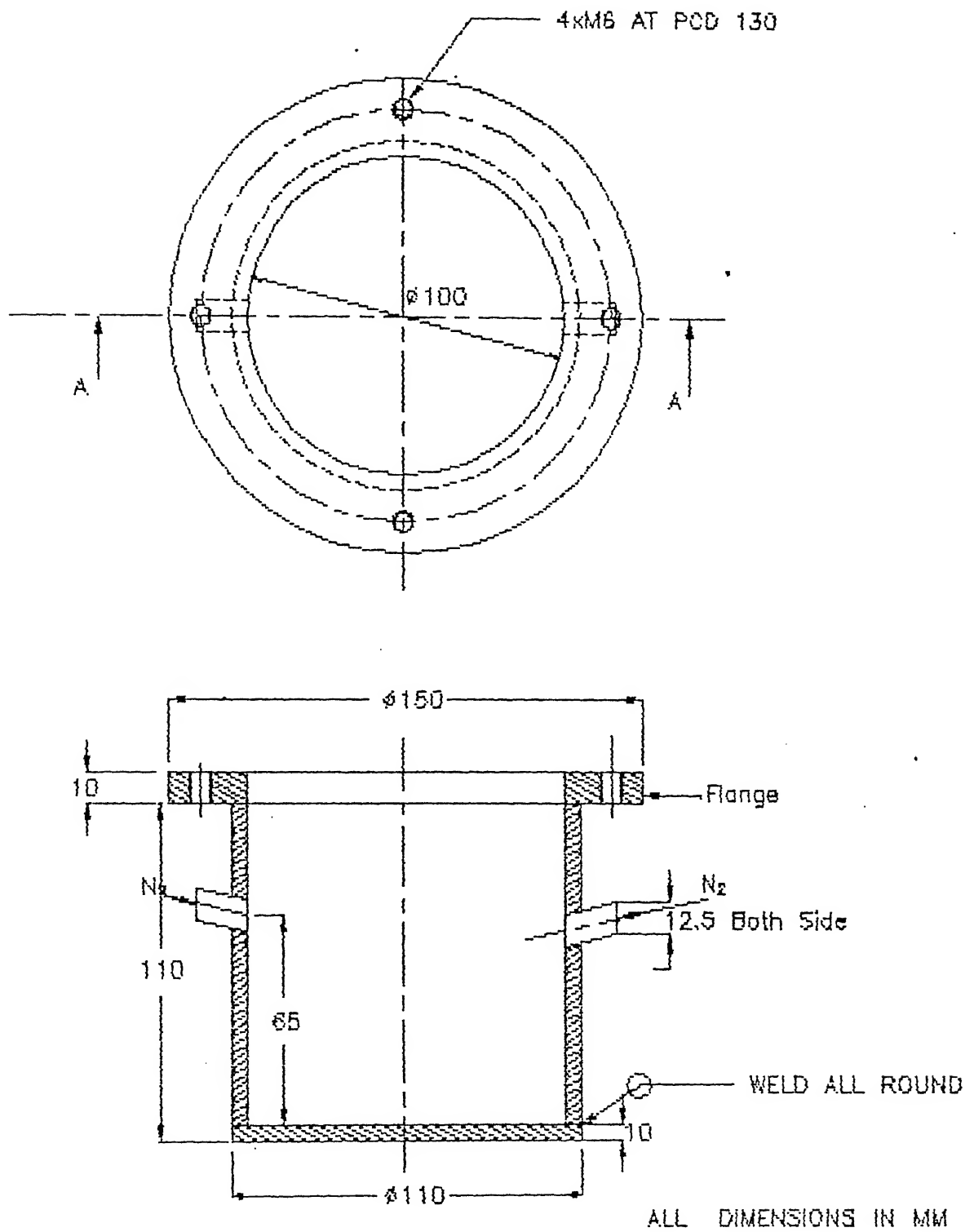
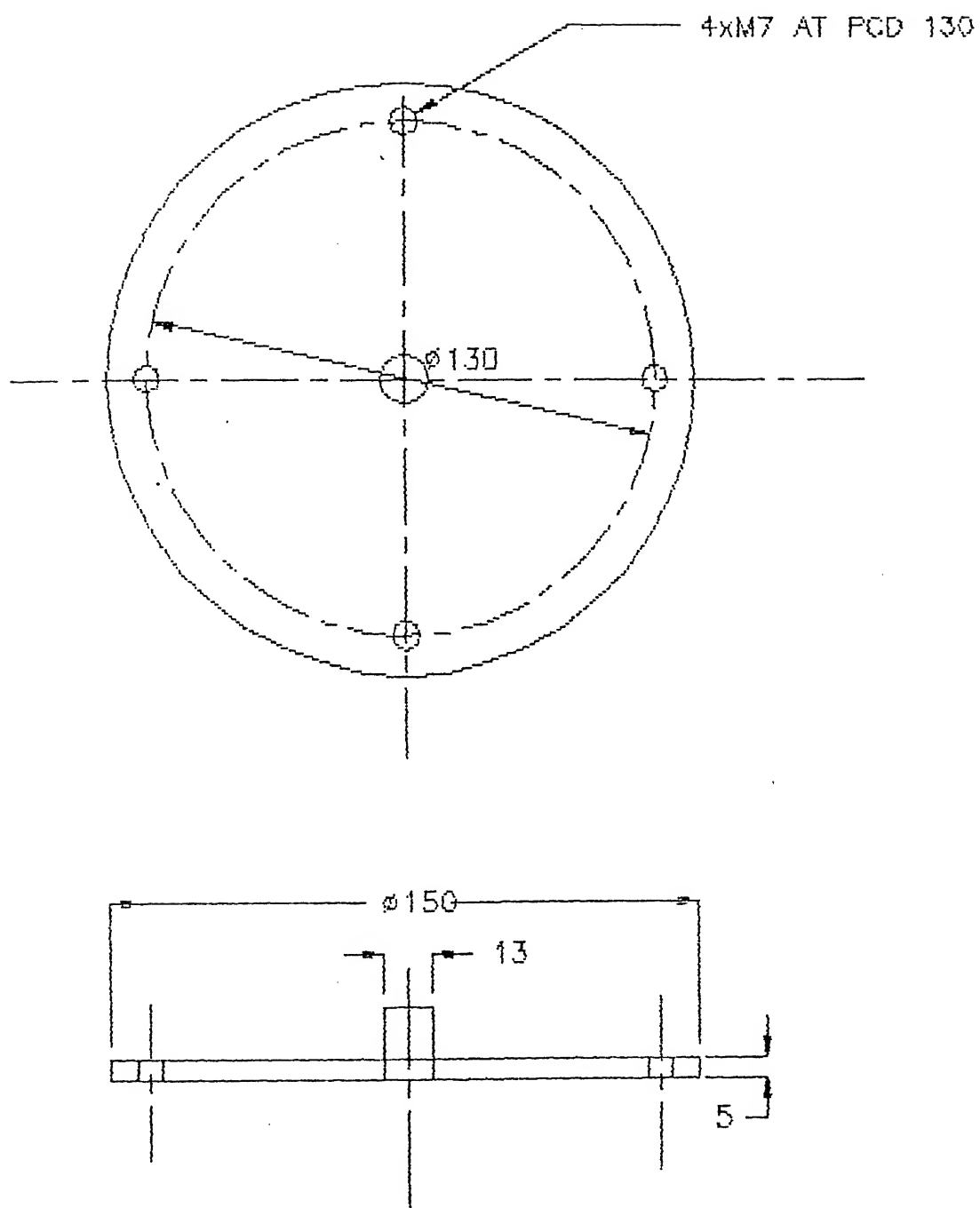


Fig.2.1 Nitrogen Chamber



ALL DIMENSIONS IN MM

Fig.2.2 Cover Plate of Nitrogen Chamber

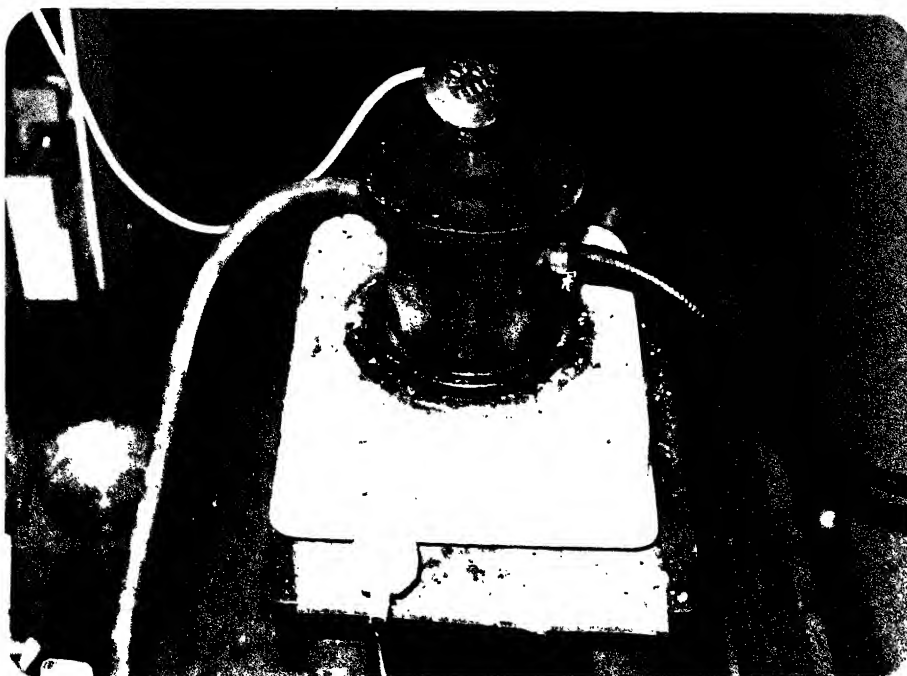


Fig.2.3      Photograph of Nitrogen Chamber Assembly Used for preparing epoxy CTBN mixture.

## 2.7 ORIENTATION OF FIBRES IN THE LAMINATE

The orientation of the glass fibre reinforced epoxy laminate is  $[0/45/-45/90/90/-45/45/0]_s$ . This orientation is same for both treated and unmodified laminates.

## 2.7 FABRICATION OF LAMINATE

A laminate is prepared by curing the stacked laminas under high pressure and temperature between two platens of a hydraulic press as shown in Fig. 2.4. The hand lay-up of laminate is prepared on a teflon coated glass fiber sheet (0.24 mm thick). The epoxy solution is applied on teflon coated glass fiber sheet with help of brush. Then a fabric ply (250mm X 250mm) is placed on it. Again epoxy resin is spread over the top side of the ply. By following the procedure all the sixteen fabric plies are laid over each other in the stacking sequence as discuss in Sec. 2.7. The stacking is covered on the top side with another teflon coated glass fiber sheet. The entire stacked laminate is placed between the two platens of hydraulic press.

The heater of hydraulic press is switched on and pressure is slowly increase upto 0.7 MPa such that laminate do not slip over each other. It is heated upto 140°C and the temperature measured by a thermocouple, is maintained for 210 minutes. The thermocouple is embedded near an edge of laminate. The laminate is allowed to cool down to room temperature at constant pressure. The laminate under pressure was left in the hydraulic press for 24 hours for full curing.

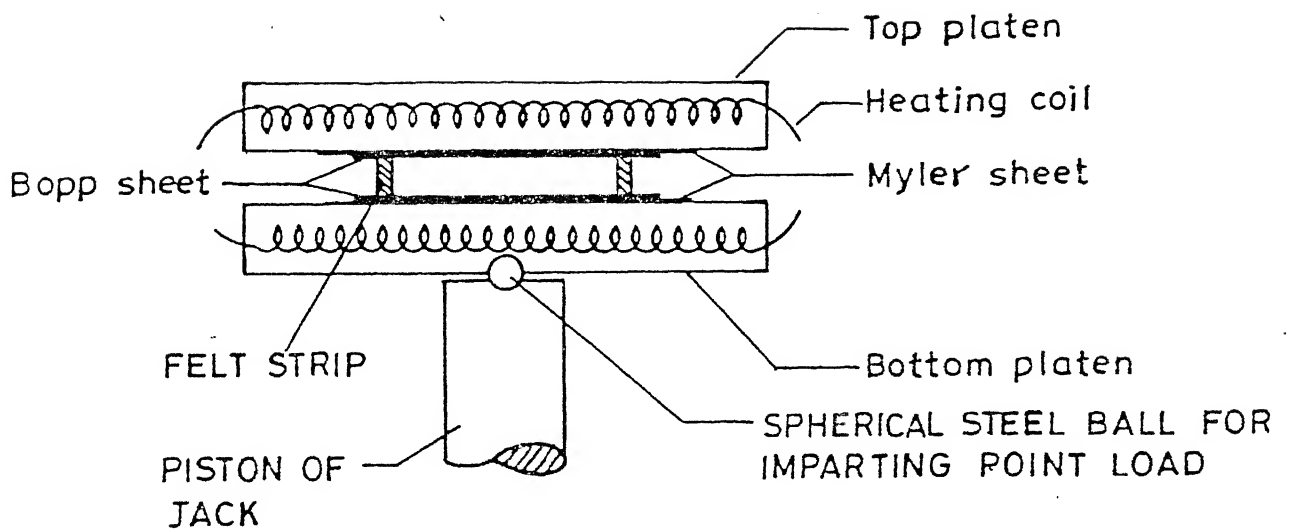


Fig.2.4      Fabrication of laminate



solution(CTBN + epoxy + triphenylphosphine), carboxylic salt is initially formed between carboxylic group of CTBN and triphenylphosphine. Further esterification reaction takes place between this salt and the epoxide group of epoxy resin to produce epoxy terminated butadiene acrylonitrile elastomer. The reaction of epoxy CTBN adduct with epoxy curing agent (HT 976) is similar to normal epoxy curing agent reaction. As the result of this reaction the rubbery phase begun to precipitate before full gelation of resin.

At any cure- temperature , the resin rubber mixture illustrates passes successively through phase separation, gelation of resin rich phase and vitrification of resin. Both gelation(conversion of branched molecules in finite molecular weight) and vitrification(formation of glassy solid from low molecular weight liquid or rubber state) prevents further phase separation during resin curing. It is therefore essential to ensure that the miscibility characteristics of resin and rubber lead to high degree of phase separation before either of gelation or vitrification. The phase separation can also continue in rubber rich phase, which remain uncross-linked above it own glass transition temperature ( $T_g$ ). Resin precipitated from this phase may produce subinclusion within rubber particles or form rubber shell around particle. The subinclusion increases the effective volume fraction of rubber particles. Thus, it has been observed in resin rubber must go through the phase separation for toughening of resin. If rubber remain in solution, it will act as plasticizer, reducing  $T_g$  of rubber but not necessarily increase its fracture toughness. Rather it reduces some mechanical properties like modulus.

## 2.9 TOUGHENING MECHANISM



It is generally accepted that two phase polymer systems such as rubber modified plastic forms toughened engineering plastic. This is due to their possession of several mechanisms for deformation which can dissipate strain energy that would otherwise be available to extend an existing flow or crack. The principal toughening mechanisms are believed to involve shear yielding and crazing matrix material, interaction between shear yielding and crazing, and the diversion and multiplication of the growing crack itself. The crazing may be visualised as process of forming a cavity, containing joined stalactites and stalagmites. The presence of rubber tends to greatly encourage the development of a dilational stress field at plastic rubber interface, so that crazing tends to be much more common in rubber modified plastics than in, for example, glass filled plastics. Sayre et al. (1984) has predicted a model of rubber toughening as :

$$\Delta G_{Ic} = \left(1 - \frac{6}{\lambda^2 + \lambda + 4}\right) 4TV_p$$

where T = tearing energy of rubber particles

$V_p$  = volume fraction of phase separated rubber

$\lambda$  = extension ratio at failure

= ratio of total length of stretch rubber particle to particle diameter

From above discussion the four possible contribution to fracture energy can be identified with rubber particle crazing are :

- (i) plastic work of craze formation
- (ii) Visco-elastic work of craze extension under stress
- (iii) Surface energy of the holes created (stress whitening)
- (iv) Bond breakage between matrix and fibre

When a stress is applied to a polymer specimen, the first deformation typically involve is shear flow of the polymer molecules pass one-another. Eventually, as the strain(or

stress) increases, a crack may begin to form; presumably at a flaw of some kind and then propagate at an ever-increasing rate upto very high value at which catastrophic failure occur. In this process presence of rubber phase increases the yielding of matrix. The triaxial tension induced due to rubber inclusion permit the shear yielding in matrix and, also  $T_g$  of matrix is lowered to permit cold drawing of matrix.

Merz(1956) suggested that on application of strain(or stress) many cracks are formed but rubber particles spanned the cracks and hinder further crack growth. The higher energies required to fracture are attributed to the ability to absorb a great deal of energy by stretching of rubber particles.

Kesk et al. (1960) suggested that rubber particles serve as stress concentration and thus initiate the development of many micro-cracks around the rubber particles. This helps in increasing the energy dissipation area, hence the energy required for failure increases. If the rubber particles are significantly close together, the interaction of the stress field may increase craze density and hence increase the fracture toughness.

Jordon et al. (1989) studied the effect of matrix resin composition on pure resin tougheners and on delamination fracture tougheners as well. It was observed that the increase in delamination fracture resistance of composite as a whole is not commensurate with the increase in matrix toughness. The plausible causes may be :

- (i) Constraint in resin deformation due to presence of brittle fibres.
- (ii) Reduced deformation in zone around the crack-tip due to fibres acting as rigid fillers.

## CHAPTER 3

# IMPACT DAMAGE AREA TOLERANCE

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### 3.1 INTRODUCTION

During the past decades, significant progress has been made in developing advanced composites possessing high strength, high modulus and low weight. As result composites have been employed as structural material in aircraft, missiles and space vehicles. But the advantage of composites over metals are overshadowed due to their poor response to impact loading. This has restricted the application of composites to structure which are subjected to hostile environment such as foreign object impact.

It has been found that even very low velocity impact causes considerable damage to composite laminate. For example, during the take off or landing of aeroplane run away debris continuously damages the wing and fuselage if they are made of FRP laminates. Hail storms are known to cause impact damage in FRP laminates. Also during repairing if a tool is dropped, it may cause damage. Many times such damage cracks are present

in the interior of a laminate which can not be seen by naked eyes. This makes the impact response of FRP further vulnerable.

This poor impact response of composite laminate requires a search for new toughened composite material. so in present work a attempt has been made to improve the impact tolerances of glass/epoxy laminate by modifying epoxy resin with the help of liquid rubber(CTBN). The damage area is prepared and tested in the same conditions(in the air gun facility at I.I.T. Kanpur). The impact damage area is used as a criteria for comparing the damage tolerance.

### 3.2 ENERGY DISSIPATION MODES

The response of composite material to impact loading is very intricate. There have been observed various mechanism acting at impacted point e.g. shear cut out of plug; fiber breakage; fibre- matrix debonding; stretching and pullout of fibres; delamination; matrix deformation and breakage. Thus there are various ways by which incident energy of the impact gets dissipated. These different ways can be summarised as:

$$E = E_f + E_s + E_r + E_d + E_o$$

where

$E$  = total energy of impactor.

$E_f$  = energy lost in flexural vibrations.

$E_s$  = energy absorbed in the support.

$E_r$  = energy of rebounded impactor.

$E_d$  = energy dissipated in damage zone.

$E_o$  = other form of energy.

Further  $E_d$  can be divided as :

$$E_d = E_{fb} + E_{del} + E_{mc} + E_{do}$$

where

$E_{fb}$  = energy dissipated in fibres breakage.

$E_{del}$  = energy dissipated in delamination

$E_{mc}$  = energy consumed in matrix cracking.

$E_o$  = any other form of energy dissipation such as debonding etc.

None of the above said form of energy dissipation solely responsible for incident energy absorption rather their combination acts as dissipation media. Critescu et al.(1975) observed that delamination is one of the main failure mechanisms in impact. Takeda et al.(1982) observed in a separate investigation that two main failure modes of impact damage were delamination and transverse crack. Cantwell and Morton (1985) investigated the modes of failure in carbon fibre reinforced epoxy laminate and found that laminate stiffness was a dominate factor and it controls the modes of failure. Kumar and Narayanan (1990) found that energy absorbed by interlaminar delamination is considerably less than the total energy dissipated in the panel. Takeda et al. (1981) investigated the wave propagation in the impacted panel and found that a flexural wave is mainly causes the delamination.

In the impact and transverse loading, the contribution of fibres are less because of their

brittle nature and poor strength along transverse direction. Thus it has been observed that in impact loading, matrix deformation and delamination are main mechanisms for impact energy absorption.

### **3.3 EXPERIMENTAL TECHNIQUE**

#### **3.3.1 Specimen**

The 150mmX150mm and 180mmX180mm laminates are prepared from both rubber modified and unmodified epoxy/glass fibres as discussed in Sec.2.8. The same curing and manufacturing conditions are used for both laminates.

#### **3.3.2 Experiment Set-up and Procedure**

The most common test for impact testing are Izod and Charpy test. The limitations to these methods lie in their inability to provide data of basic physical significance. Hence in this study, the impact testing of specimens are performed on a air gun which can accelerates projectile of different masses at the different velocities. Thus air gun testing simulates the real world impact situation.

The schematic diagram for the experimental set-up for laminate impacting is given in Fig. 3.1 and photograph of impact experiment set up is given in Fig. 3.2. In this study, The laminates are impacted by a cylindrical projectile of length 20mm and of hemispherical nose. The projectile is made of mild steel and weighs 11.6gm. The

laminate is rigidly fixed by its edges with the help of clamp rings as shown in Fig.3.1. The projectile is accelerated horizontally inside a barrel of 11mm bore and 3.65m length with the help of compressed nitrogen gas. The pressure of gas can be varied with the help of a control panel to get a desired velocity of projectile. The barrel is positioned such that the projectile hits at the centre of specimen laminate. A 'O' ring is inserted at the rear end of the projectile so that nitrogen gas does not leak-out through the sides of projectile when it is being accelerated in the barrel of the airgun.

To get the velocity of the projectile just before the impacting the laminate, three light beams are generated with the help of three bulbs and each beam is fallen on a photo-diode. The bulbs and the photo-diodes are housed in a steel block at the end of the barrel such that the beams are cut by the projectile on way to its impact on the specimen laminate. The photo-diodes are connected to a time counter having two time-windows to measure time which is of 1 micro-second accuracy. The distance between two adjacent beams is kept at 15mm. When the projectile cuts the first light beam, the corresponding diode give a signal to the time counter in which counting in the first time window initiates. When the second beam is cut by the projectile the corresponding diode signal stops the time counter in the first window and starts the second time window to count time. Similarly cutting the third beam of light stops the second times. The signals of the diodes are carried to the time counter through a proper electronic circuit for the purpose. Thus first and second window give the time taken by the projectile to travel from first beam to second beam and second beam to third beam respectively. With known distance between two adjacent beams, velocity of the projectile is determined.

### **3.3.3 Data Reduction Method**

The impact damage tolerances of specimens are deduced from visual damage area measurement. In this method, the specimen after the impact is inspected in front of a source of flush light such as electric bulb and damage area is marked. Then the damage area of laminate is measured with help of planimeter. This damage area is used as a parameter for comparing the impact tolerances of modified and unmodified laminates.



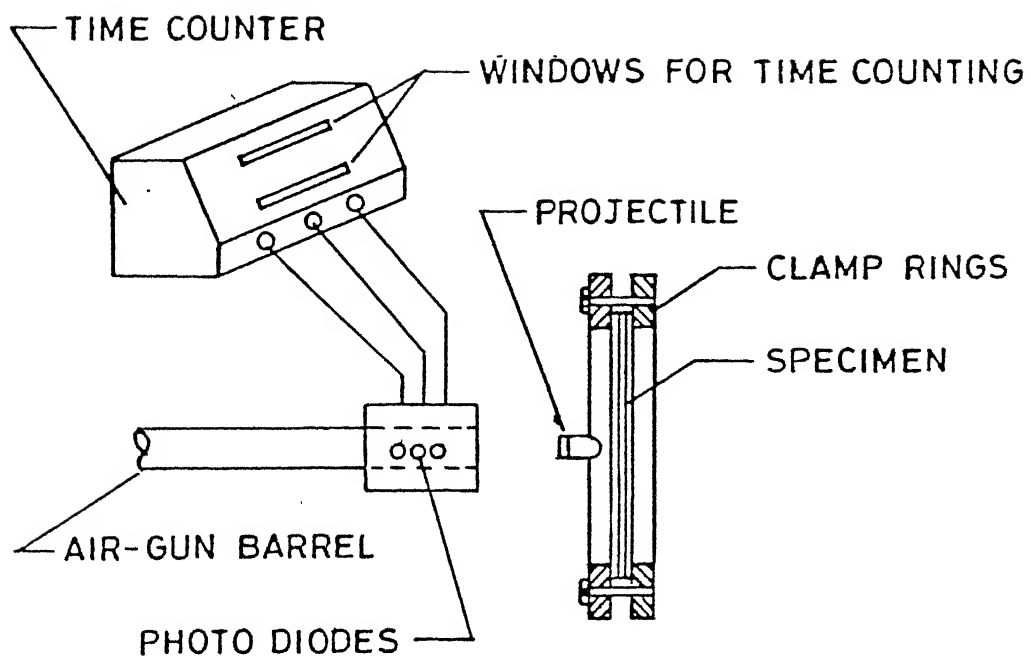


Fig.3.1 Schematic diagram of experimental set up for laminate impacting.

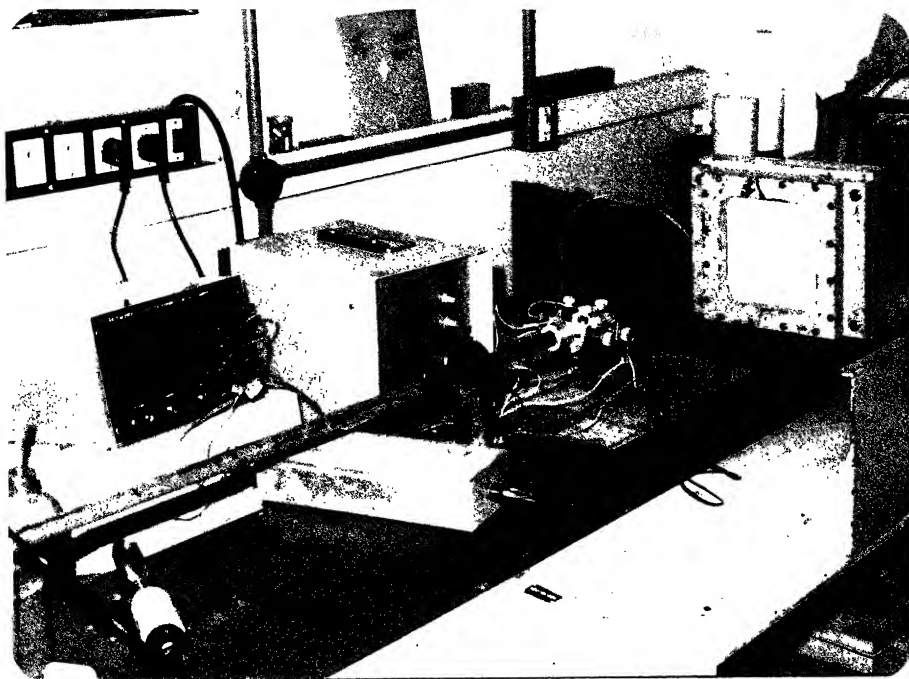


Fig.3.2      Photograph of impact test experiment set up.

### 3.4 RESULT AND DISCUSSION

Two sets of laminate, one of chemically modified and other chemically unmodified were impacted for a range of velocity by a projectile. In all experiments the projectile does not penetrate through the laminate. Table 3.1. shows the damage area of unmodified laminate for different velocities and impact energy whereas Table 3.2. shows the same for modified laminates. The data of above Table 3.1 and Table 3.2 shows that for a modified laminate, the damage area is approximately 60 % of the damage area of unmodified laminates for same impact energy.

Fig.3.3. shows the cumulative plot between damage area vs impact energy of both modified and unmodified specimens. For damage area vs impact energy plot a best fit curve has been determined with the help of linear regression method. The following best fit curves are deduced from regression method

$$A = 0.14 E^{1.389} \quad (\text{rubber modified specimens})$$

$$\text{and } A = 0.26 E^{1.37} \quad (\text{unmodified})$$

where

$$A = \text{impact induced damage area in cm}^2$$

$$E = \text{incident impact energy in J}$$

Micrographs of fractured surfaces have been taken to know the mechanisms responsible for improving damage area performance of chemically modified laminate over chemically unmodified laminate in the impact loading. The electron scanning micrographs of fractured surface of both the laminates are shown in the Fig.3.4, Fig. 3.5 and Fig .3.6.

Fig.3.4.a shows micrograph of fractured surface of unmodified laminate. The matrix cracking and debonding between fibre and matrix is clearly seen in this micrograph. In comparison of unmodified laminate the chipping of matrix is also observed. The micrograph of fractured surface of modified laminate is given in Fig.3.4.b. It shows the ductile behaviour of modified matrix under impact loading. The chipping of matrix and debonding between fibres and matrix are also seen to much less extent. Fig. 3.5.a. shows that in the unmodified laminate, fibre breakage and severe matrix cracking take place under the impact loading. The impact induced crack is also seen to travel across the whole thickness of unmodified laminate. While Fig. 3.5.b. shows that for modified laminate no fibre breakage takes place and the damage of matrix is also not as much as of unmodified laminate. Similar failure mechanisms are also evident from Fig.3.6.a for unmodified and from Fig. 3.6.b for modified laminate except that matrix chipping is observed in the case of unmodified laminate.

It is felt that there are two possible causes of damage area reduction under impact loading of chemically modified laminate over unmodified laminate :

(i) As the interlaminar crack propagates stretching and tearing of elastomer particles occurs. Also rubber particles bridge the gap between the fractured surfaces and reduces the crack opening displacement making the matrix tough. These rubber particles are stretched to large strain before tearing takes place. Thus as compared to unmodified epoxy specimens modified specimens absorbed large energy.

(ii) Matrix of modified epoxy is less brittle and deforms in ductile manner.

### 3.5 CLOSURE

The aim of this chapter was to improve the impact induced damage area of polymer composite laminate by chemical treatment of lamimante. The impact test has been carried out for both modified and untreated laminates. The impact induced damage area of modified laminate was found about 60 % less than damage area of untreated laminate for same level of impact energy.

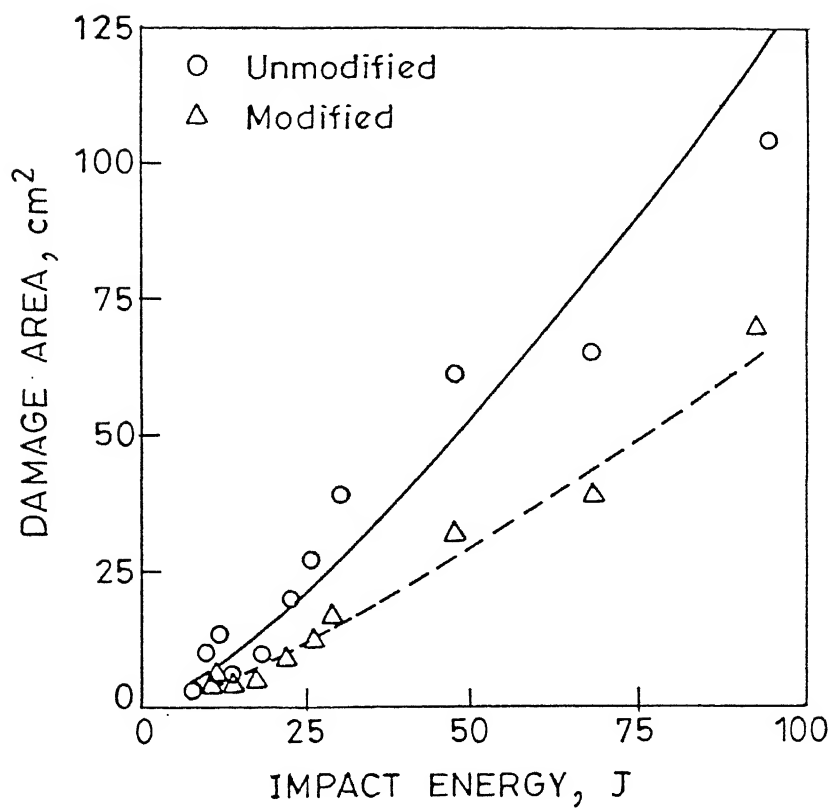


Fig.3.3 A cumulative plot between damage area vs. impact energy of both unmodified and modified specimens.

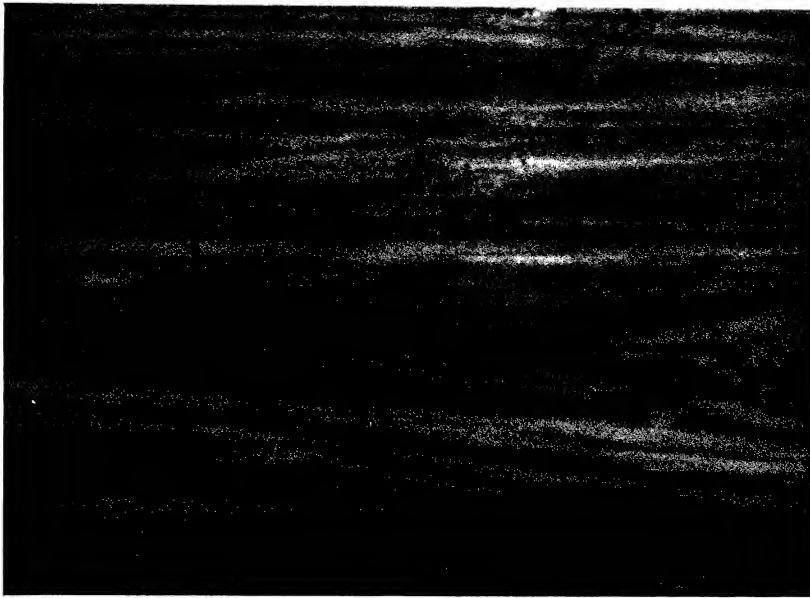


Fig.3.4.a Microphotograph of fractured surface of the unmodified specimen Number IU-9.

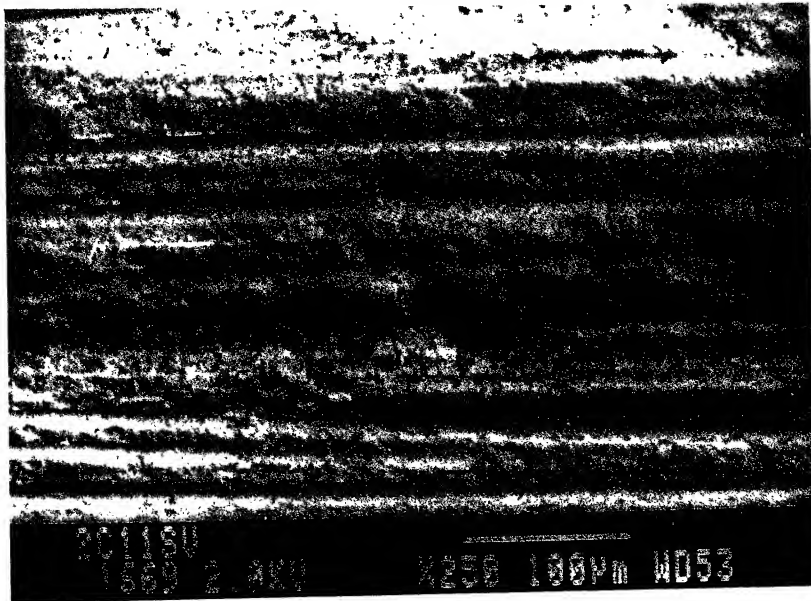


Fig.3.4.b Microphotograph of fractured surface of the modified specimen Number IM-9.



Fig.3.5.a Microphotograph of fractured cross section of the unmodified specimen Number IU-6.

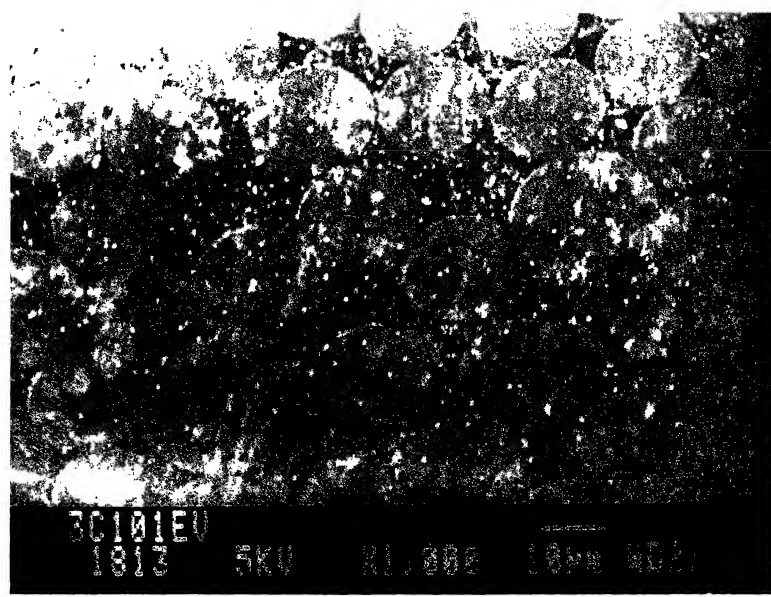


Fig.3.5.b Microphotograph of fractured cross section of the modified specimen Number IM-6.



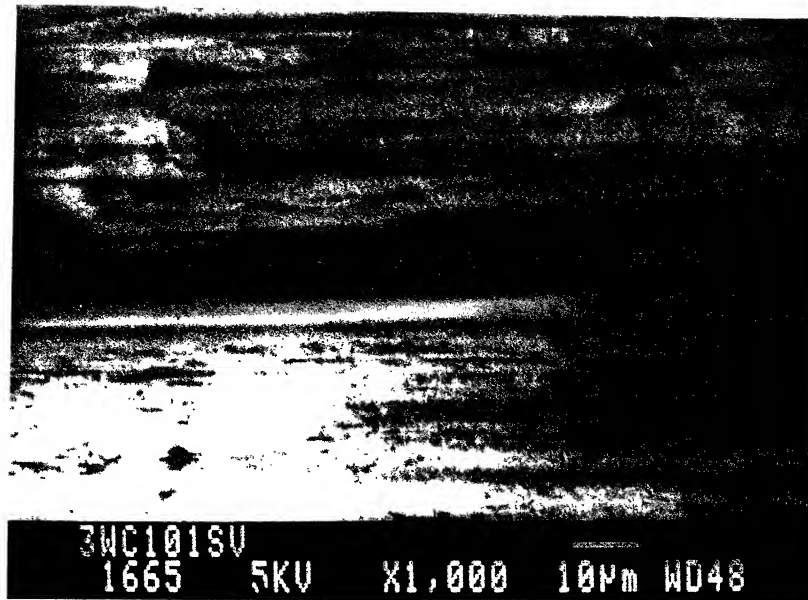


Fig.3.6.a Microphotograph of fractured surface of the unmodified specimen Number IU-6.

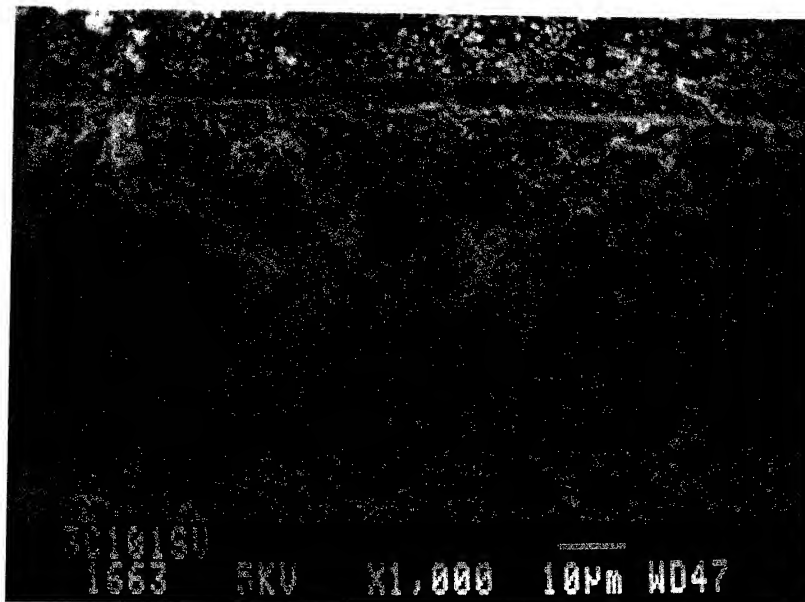


Fig.3.6.b Microphotograph of fractured surface of the modified specimen Number IM-6.

**Table 3.1 Impact Induced Damage Area For chemically Unmodified Laminates**

Expt. number	Impact velocity (m/s)	impact energy (Nm)	Damage area (cm <sup>2</sup> )	% Fibre Volume Fraction
IU-1	36.3	7.8	2.8	66
IU-2	40.8	9.9	9.6	60
IU-3	44.6	11.9	13.0	66
IU-4	48.3	13.9	5.6	64.5
IU-5	55.0	18.1	9.3	71.8
IU-6	61.4	22.5	19.5	74
IU-7	64.9	25.7	27.0	63
IU-8	71.2	30.2	39.0	68
IU-9	89.3	47.5	61.0	65
IU-10	106.6	67.7	65.0	67
IU-11	126.0	93.7	104.0	63.4

**Table 3.2 Impact Induced Damage Area for Chemically Modified Laminates**

Expt.number	Impact velocity (m/s)	Impact energy (Nm)	Damage area (cm <sub>2</sub> )	% Fiber volume fraction
IM-1	40.7	9.8	4.5	53
IM-2	42.6	10.8	4.0	52.5
IM-3	44.2	11.6	6.5	51
IM-4	48.4	14.0	4.9	54.8
IM-5	54.0	17.4	4.9	60.2
IM-6	60.6	21.9	9.0	62.5
IM-7	66.0	26.0	12.4	55
IM-8	69.4	28.7	17.0	58
IM-9	89.4	47.6	32.0	53
IM-10	106.9	68.0	39.0	56.3
IM-11	124.9	92.0	70.0	56.4

### MODE I INTER LAMINAR FRACTURE TOUGHNESS

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#### 4.1 INTRODUCTION

Composite materials are generally anisotropic and having laminated structure which makes them prone to interlaminar failure during impact loading. Moreover, laminate do not have through the thickness reinforcement of fibres and a layer of brittle matrix material exists between the two laminae. This make the composite further susceptible to inter ply failure.

In chapter III, the impact damage area of chemical treated laminate was found to less than that of untreated laminate for same incident impact energy. Cristescue et al. (1975) has reported that Delamination constitutes the major part of impact damage. Hence the effect of chemical treatment on delamination resistance of laminate is investigated to know the mechanisms responsible for impact damage area improvement for treated laminate. Therefore, delamination resistance of both chemically treated and untreated laminates is investigated in mode I loading and is presented in the present

chapter. The delamination resistance in mode II loading of both treated and untreated laminates is also investigated and is presented in chapter 5.

## 4.2 ENERGY RELEASE RATE

In linear fracture mechanics (LEFM), there are several parameters employed to predict the onset of crack growth. These parameters include energy release rate, stress intensity factor, crack opening displacement. The stress analysis in the vicinity of a crack tip in a composite material is difficult because of local heterogeneity and anisotropy. Thus it becomes a common practice to characterise interlaminar fracture with energy release rate  $G$ . The energy release rate  $G$  is defined as energy release per unit area of extension of crack growth. The value of energy release rate  $G$  at which crack extends is called the critical value and denoted by  $G_c$ . This quantity is based on energy consideration and is mathematically well defined as well as physically measurable in experiments.

Energy balance for a cracked body can be given as

$$\phi = U - W \quad (4.1)$$

where  $U$  is the elastic strain energy and  $W$  is the external work.

The energy release rate ( $G$ ) is defined as

$$G = -\delta\phi/\delta A \quad (4.2)$$

where  $\phi$  is the potential energy and  $A$  is crack area.

Compliance is defined as

$$C = u/p$$

where  $u$  is the displacement of load  $P$ .

It can be shown that (Broek 1987)

$$G_I = \frac{p^2}{2} \frac{\delta c}{\delta A} \quad (4.3)$$

$$= \frac{P^2}{2b} \frac{\delta C}{\delta a} \quad (4.4)$$

where  $b$  is the width and  $a$  is the crack length of specimen.

For cantilever beam of length  $a$ , under load  $P$  at the free ends of cantilever, the displacement,  $\delta$  is given by :

$$\delta = \frac{Pa^3}{3EI} \quad (4.5)$$

where  $E$  is the Young's modulus and  $I$  is the moment of inertia of cross-section for DCB specimen under mode I load  $P$  as shown in Fig.4.1. Since each cantilever's end are displaced by  $\delta$ . Therefore, total displacement  $u$  is given by,

$$u = \frac{2Pa^3}{3EI} \quad (4.6)$$

Compliance  $C$  can be written as

$$C = \frac{2a^3}{3EI} \quad (4.7)$$

On differentiating above equation w.r.t.  $a$

$$\frac{\delta C}{\delta a} = \frac{2a^2}{EI} \quad (4.8)$$

Substituting Eq. 4.8 into Eq. 4.4

$$G_I = \frac{P^2 a^2}{EIb} \quad (4.9)$$

For critical load  $P = P_c$ ,  $G_I$  becomes

$$G_{Ic} = \frac{P_c^2 a^2}{EIb} \quad (4.10)$$

### 4.3 EXPERIMENTAL TECHNIQUE

For determining the mode I interlaminar fracture toughness, compliance method using DCB specimen under fixed grip condition has been used.

#### 4.3.1 Specimen

In present study specimen used is double cantilever beam (DCB) of following dimensionas shown in Fig. 4.2.

Length  $L = 230\text{mm}$

Width  $b = 30\text{mm}$

Precrack length  $a \approx 45\text{mm}$

Thickness  $= 3\text{mm}$

The DCB specimen of above given dimensions is prepared by hand casting method as describe in Sec.2.8. For these specimens precracking is required which is achieve by placing a thin sheet of BOPP at the mid plane of laminate during casting of laminate.

#### **4.3.2 Experiment Procedure**

Cantilever ends of DCB specimen are pulled apart in a tensile machine(Instron, 10 tonne capacity) with top cantilever attached to the fixed jaw of machine as shown in Fig. 4.3. The lower cantilever is pulled down in displacement control mode at very slow cross head speed of  $1\text{mm/min}$ . The specimen is always kept horizontal during testing by suspending its other end with a thread. Load cell used was  $10\text{ kN}$ (maximum capacity) a real time display of load vs. deflection is obtained. As the cantilever ends are pulled apart they rotate. A hinge is provided on each side of cantilever so as to release moment cause by rotation. The hinge consists of two parts, a rectangular tab which is attached to a cantilever end and a hinge-fork which forms hinge with tab and whose top portion is designed to be gripped between the jaws of tensile testing machine. The rectangular tabs are specially designed such that they can be screwed to cantilever's ends.



For example, the top slab is screwed from bottom through four corner holes and corresponding clearance for head of the screw is provided in the bottom slab. Before loading the specimen, both side edges of specimen are painted white so as to locate the crack tip during experiment. Also a thin strip of graph paper is bonded on the bottom half of the side faces of specimen such that change in crack length can easily measured. The photograph of loaded DCB specimen is give in Fig.4.3.

The specimen was loaded in mode I and the crack is allowed to grow by 5-6 mm. The machine is stopped and unloaded till the load becomes zero. The machine is again loaded for larger crack length. The cycle of loading and unloading is repeated for 5-7 times. As shown in Fig.4.4 crack length for every cycle of loading is taken from front and back side faces using magnifying lens. The typical graph obtained in the experiment is shown in Fig. 4.4.

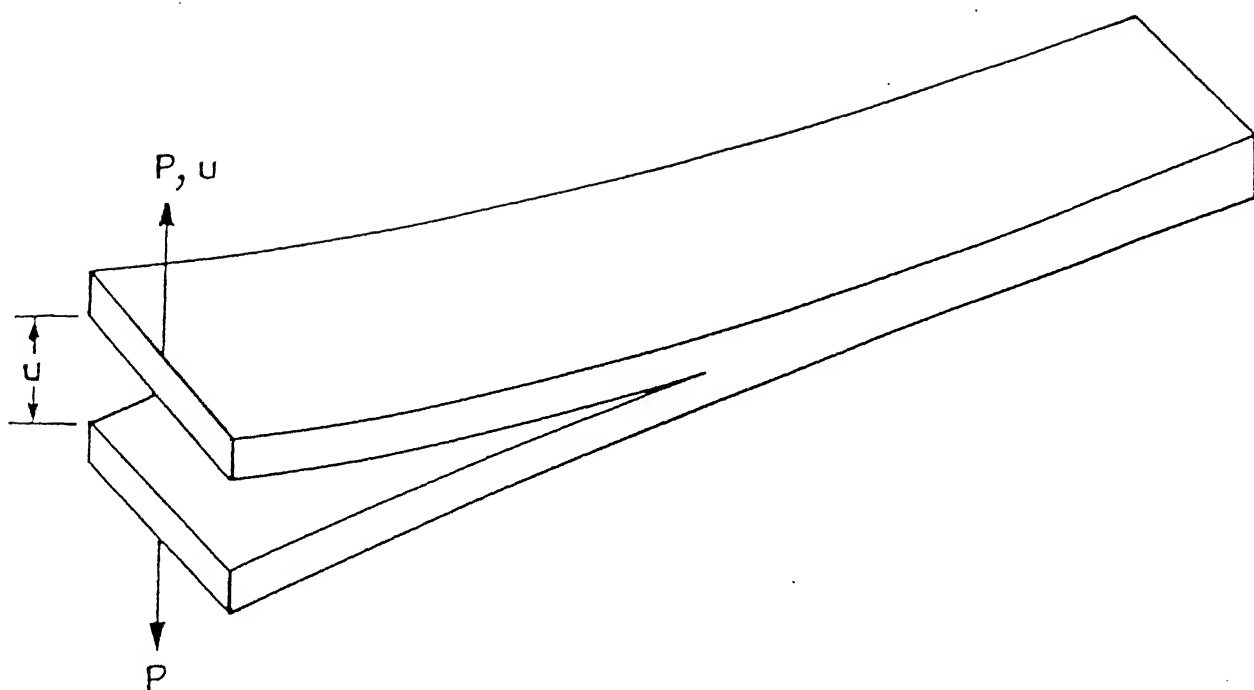


Fig.4.1 The loading configuration of DCB in mode I.

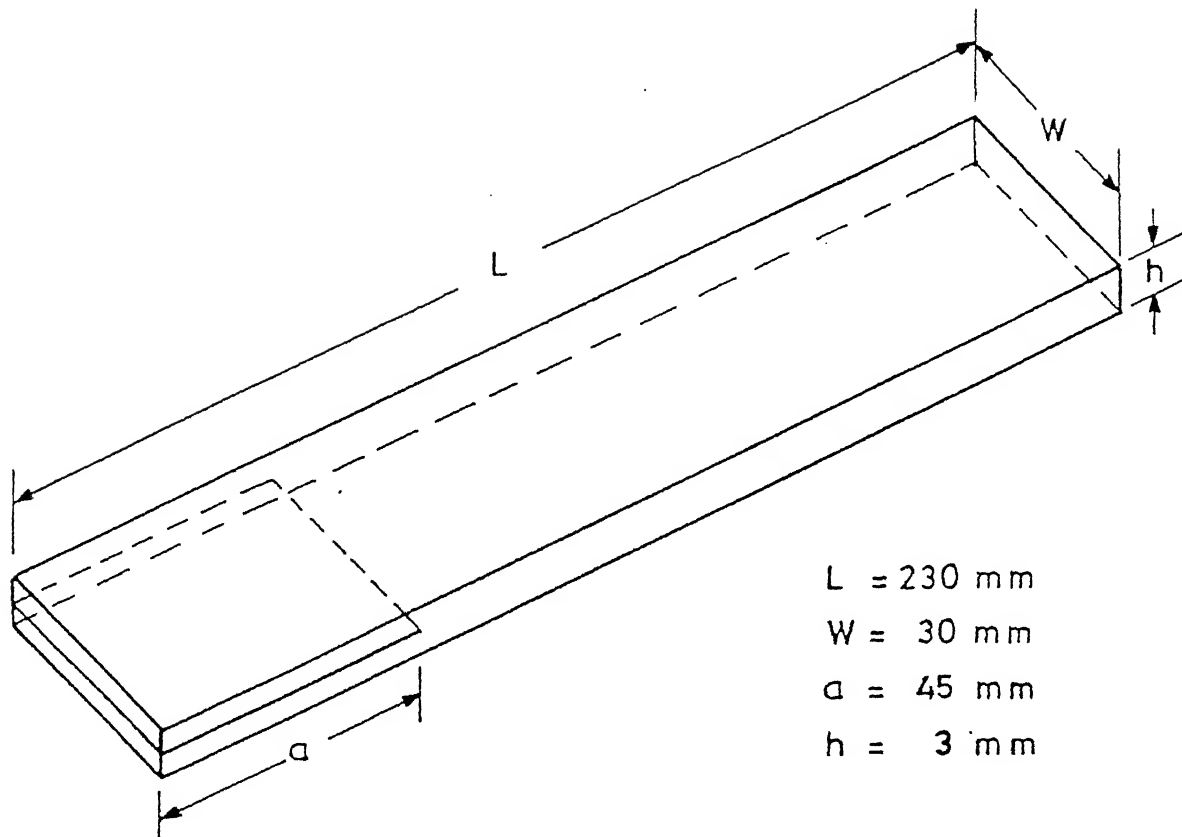


Fig.4.2 A DCB specimen with its dimensions.

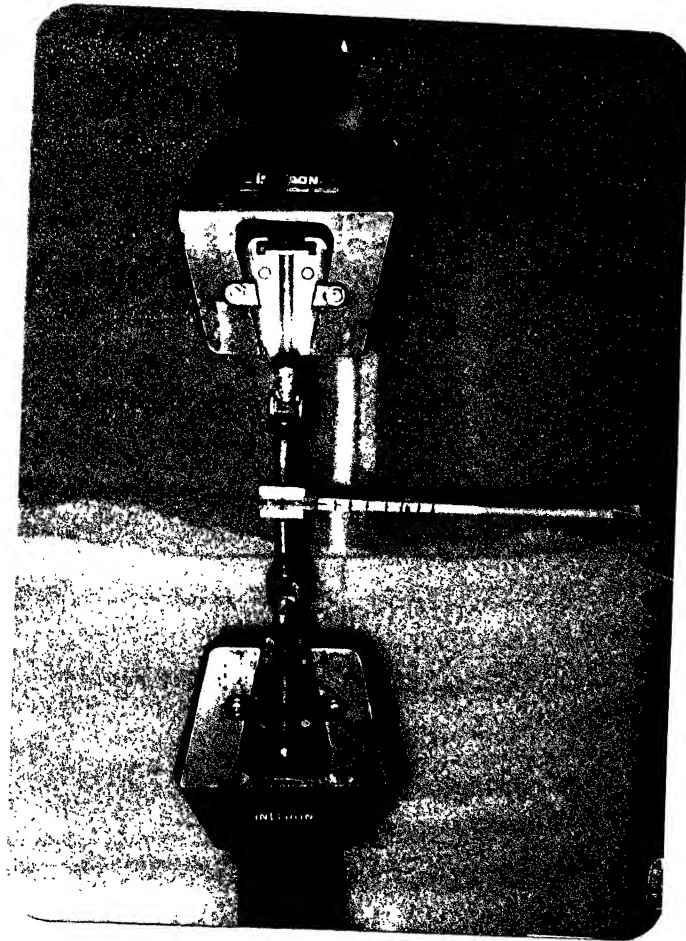


Fig.4.3      Photograph showing a loaded DCB specimen in MTS machine.

### 4.3.3 Data Reduction Method of DCB Test

The compliance method of data reduction has been used in present study. A typical load vs. displacement curve of DCB test has been shown in Fig. 4.4. For each crack length, the compliance is determined from the slope of loading part of curve and the corresponding critical load is also noted.

Equation 4.7 can be rewritten as

$$C = A_1 a^3 \quad (4.11)$$

where  $A_1$  is a constant for a given specimen and is given by

$$A_1 = \frac{2}{3EI} \quad (4.12)$$

From Equa 4.10,  $P_c$  is given by

$$P_c = \frac{\sqrt{G_{Ic} E I b}}{a}$$

which is expressed as

$$p_c = \frac{A_2}{a} \quad (4.13)$$

where  $A_2$  is constant and is equal to

$$A_2 = \sqrt{G_{Ic}EIb} \quad (4.14)$$

Eliminating EI from Eq. 4.12 and Eq. 4.14

$$G_{Ic} = \frac{3A_1A_2}{2w} \quad (4.15)$$

The values of  $A_1$  and  $A_2$  can be found out graphically or by linear regression. Taking logarithm of Eq. 4.11

$$\ln C = \ln A_1 + 3 \ln a$$

Experimental points of  $\ln(C)$  and  $\ln(a)$  are plotted on a graph and a straight line of slope 3 is fitted to the data points by hand or linear regression method (adopted in this study). The length cut by above line with ordinate of graph will give  $\ln A_1$ . A typical plots between  $\ln(C)$  vs  $\ln(a)$  for experimentally determined data points are shown in Fig. 4.5 for chemically untreated laminate and in Fig. 4.6 for treated laminate. the fitted straight lines were obtained by the linear regression method.

Similarly taking logarithm of Eq. 4.13

$$\ln p_c = \ln A_2 - \ln a$$

Again experiment data points for  $\ln(p_c)$  and  $\ln(a)$  are plotted. a line of slope -1 is fitted along these data points. The ordinate of the graph cut by this line will be equal to  $\ln A_2$ .

The graphs between  $\ln(P_c)$  vs.  $\ln(a)$  has been shown in Fig. 4 untreated laminate and in Fig. 4.8. for treated laminate.

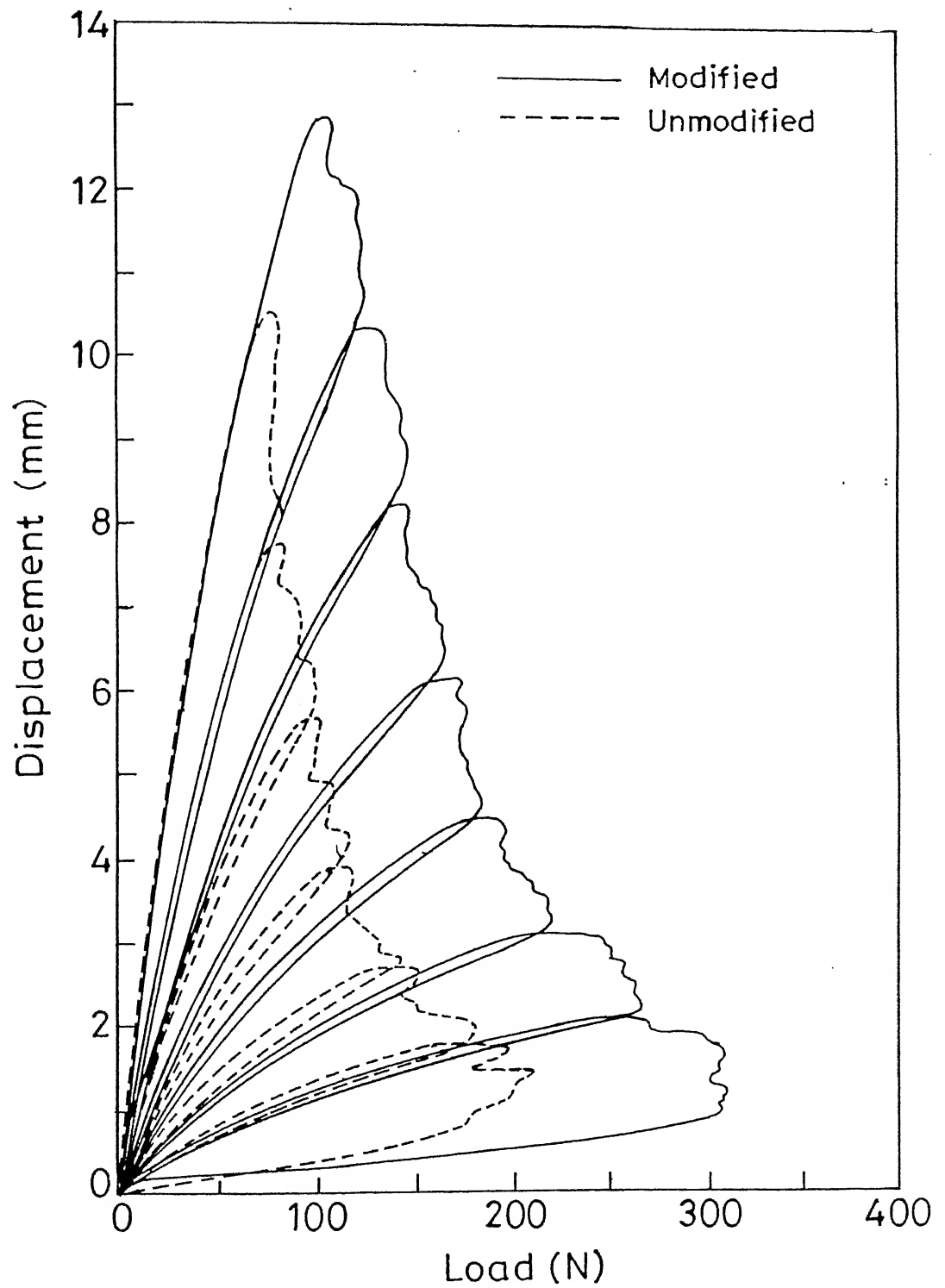


Fig.4.4 A typical load vs. displacement curve of mode I test.

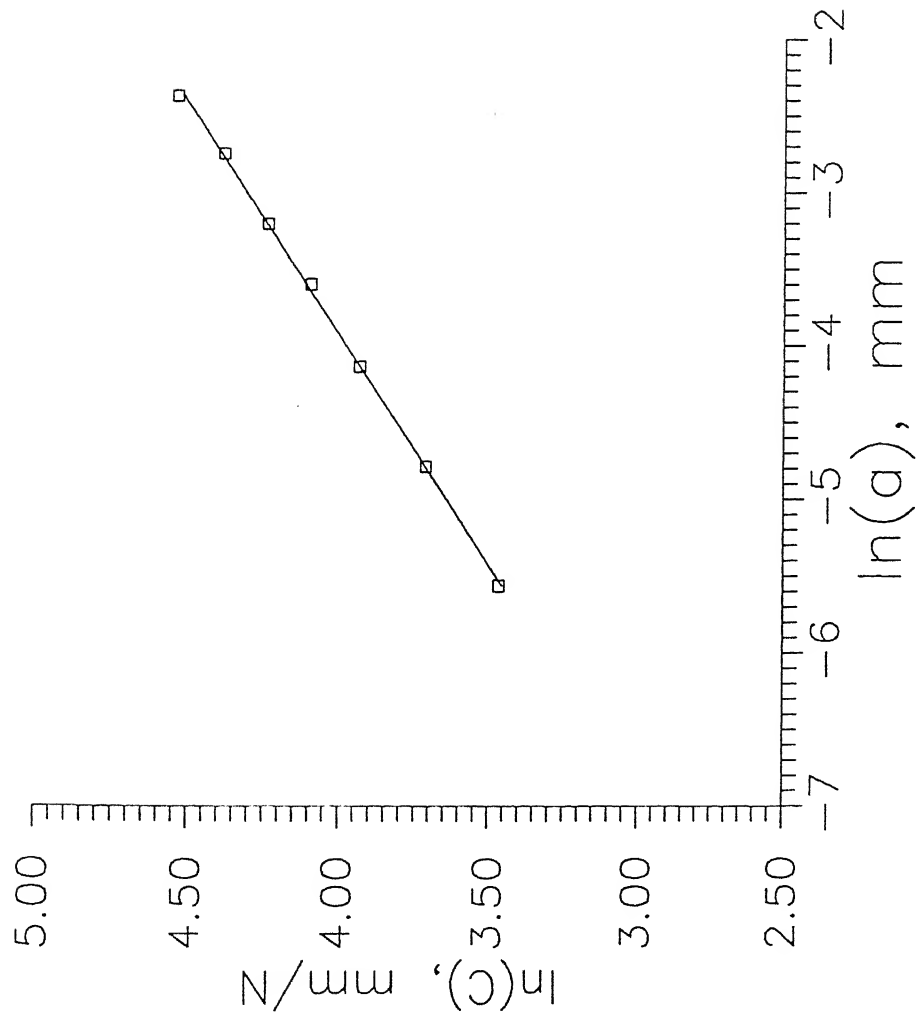


Fig.4.5  $\ln(c)$  vs.  $\ln(a)$  data fit curve for chemically unmodified laminate



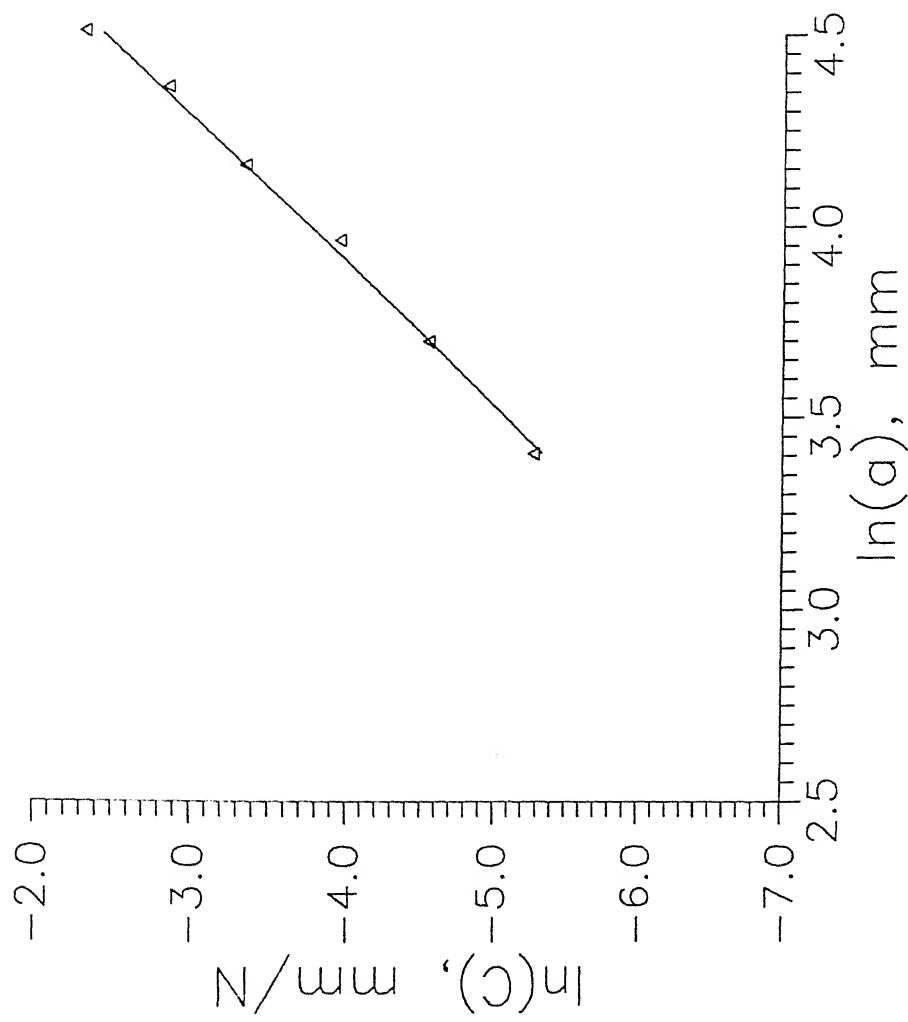


Fig.4.6  $\ln(c)$  vs.  $\ln(a)$  data fit curve for chemically modified laminate

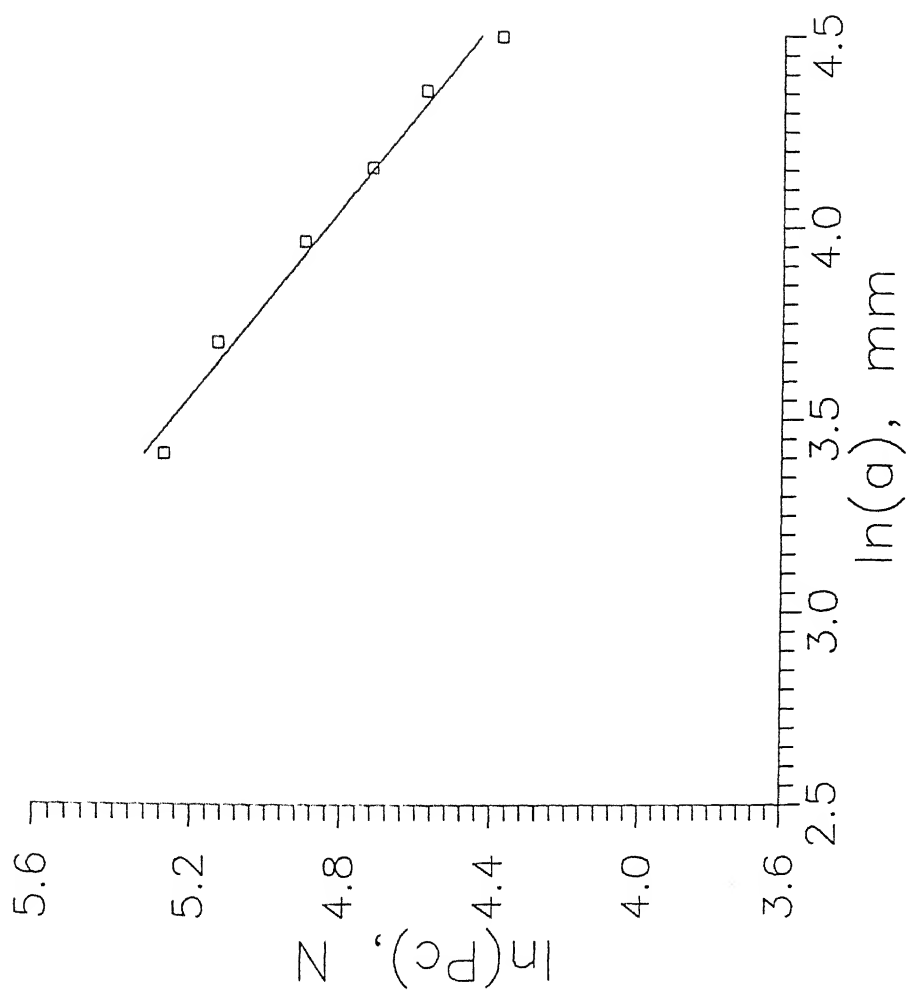


Fig.4.7  $\ln(p_c)$  vs.  $\ln(a)$  data fit curve for unmodified laminate.

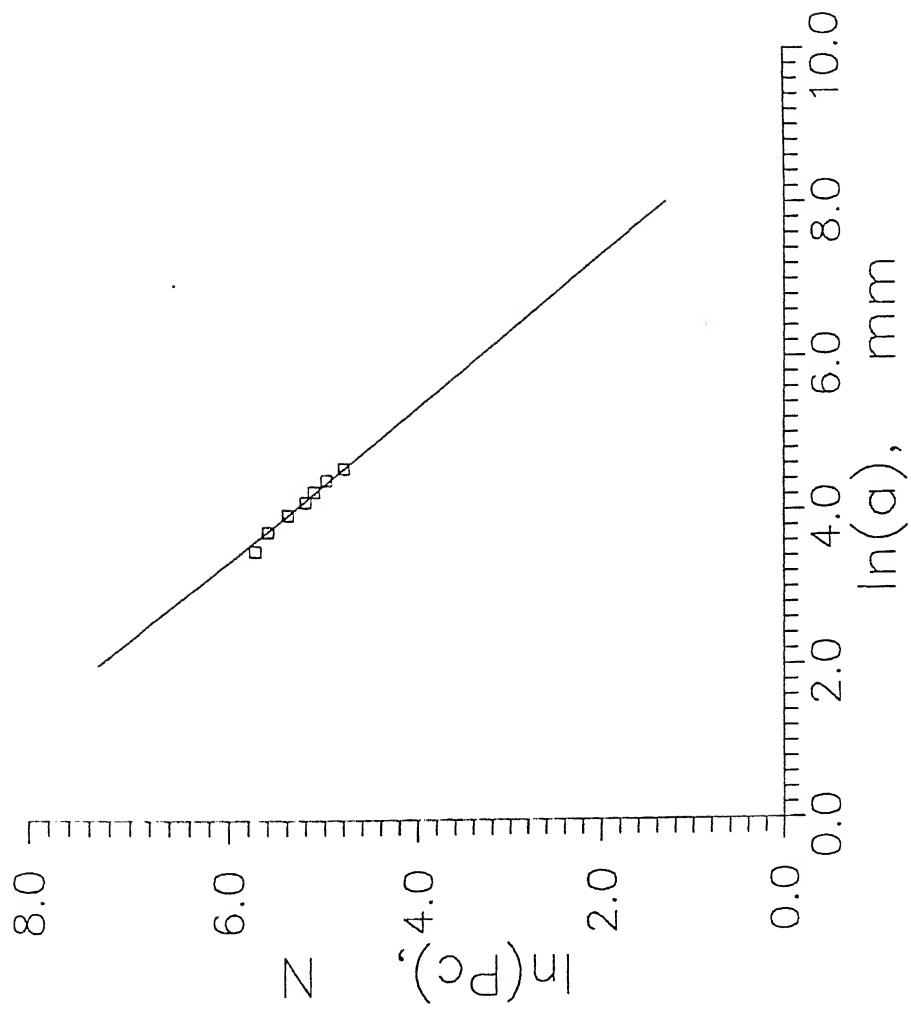


Fig.4.8  $\ln(p_c)$  vs.  $\ln(a)$  data fit curve for modified laminate.

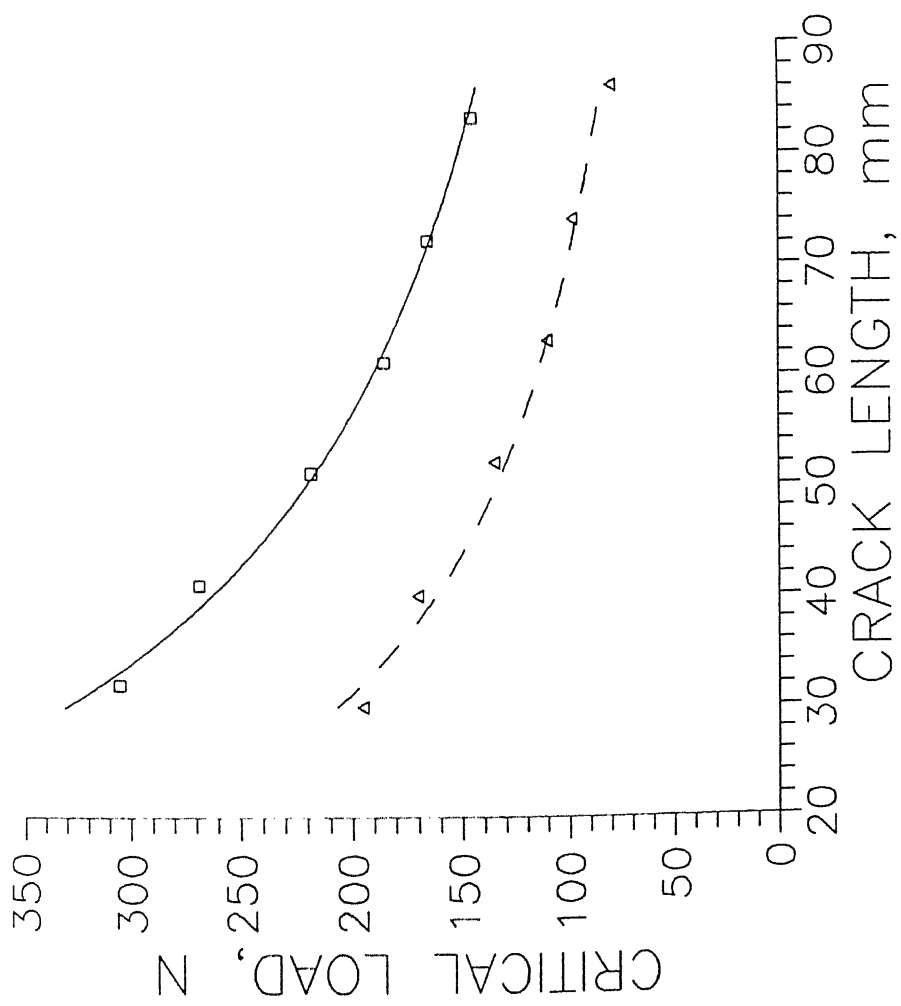


Fig.4.9 Critical load vs. crack length plot obtained from mode I testing.

#### 4.4 RESULT AND DISCUSSION

The interlaminar critical energy release rate  $G_{Ic}$  is experimentally determined for both the chemically treated and untreated specimens. The detail of specimen geometry is given in the Sec.4.3.1.and chemical treatment of specimen is given in Sec. 2.4. The detail of experiments is already discussed in the Sec. 4.3.2.

A typical displacement vs. load diagram for both the treated and untreated laminate specimens which is obtained during testing is shown in the Fig. 4.4. From this diagram, it is obvious that enclosed area between load vs. displacement curve for the chemically treated laminate is more than that of chemically untreated laminate. This shows the higher value of  $G_{Ic}$  for treated laminated specimens than the untreated laminate specimens.

A plot between critical load vs. crack lengths is presented in the Fig. 4.9 for both treated and untreated specimens. It is obvious from Fig. 4.9 that for same crack length the crack critical loads is more for the chemically treated laminate than of untreated laminate.

The interlaminar critical energy release rate  $G_{Ic}$  for chemically untreated laminates is given in Table 4.1 and for treated laminates in Table 4.2. From these tables contents it can be concluded that average  $G_{Ic}$  of treated laminate is 40% more than untreated laminate  $G_{Ic}$ . Hence it can be concluded that improvement in the mode I delamination

resistance of treated laminates plays a role in improvement of impact induced damage area of chemically treated laminates over untreated laminates.

From microscopic point of view the increase in  $G_{Ic}$  of composite laminate due to Chemical treatment can be associated with large crack tip deformation zone of treated laminate and large scale yielding of matrix material. The large crack tip deformation zone permits blunting of crack tip and this blunting decreases the local stress concentration at the tip of crack. As a result higher loads are required for crack initiation in rubber modified matrix material laminates than those of unmodified laminates. On energy consideration matrix cracking in treated laminates is more ductile and thus absorbing more energy during crack propagation.

#### 4.5 CLOSURE

The aim of this chapter was to investigate the effect of chemical treatment on  $G_{Ic}$  of laminate. The  $G_{Ic}$  of both unmodified and modified laminate was determined using DCB specimen. The average  $G_{Ic}$  of modified specimen laminate was found  $477 \text{ J/m}^2$  and average  $G_{Ic}$  of unmodified laminate was  $339 \text{ J/m}^2$ . The result shows the improvement in  $G_{Ic}$  of composite laminate due to the chemical treatment.

Table 4.1 Inter-laminar  $G_{Ic}$  for untreated laminate

Specimen number	Interlaminar $G_{Ic}$ (J/m <sub>2</sub> )	Average Interlaminar $G_{Ic}$ (J/m <sub>2</sub> )
G1U-1	386	339
G1U-2	319	
G1U-3	298	
G1U-4	356	
G1U-5	334	

Table 4.2 Interlaminar  $G_{Ic}$  for modified laminates

Specimen number	Interlaminar $G_{Ic}$ (J/m <sub>2</sub> )	Average interlaminar $G_{Ic}$ (J/m <sub>2</sub> )
G1M-1	447	477
G1M-2	445	
G1M-3	493	
G1M-4	607	
G1M-5	449	
G1M-6	420	

# MODE II INTERLAMINAR FRACTURE TOUGHNESS

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## 5.1 INTRODUCTION

A foreign body impact develops bending moments on the laminate which give rise to shear stress between two adjacent plies. The effect is more pronounced on interfaces that are close to midplane of the laminate. It is therefore worth exploring the effect of toughening on interlaminar critical energy release rate in mode II ( $G_{IIC}$ ).

Both modified and unmodified laminates are tested to determine ( $G_{IIC}$ ). The  $G_{IIC}$  of laminates are then compared to assess its improvement in impact induced delamination.



## **5.2 EXPERIMENTAL TECHNIQUE**

### **5.2.1 Specimen**

For mode II testing, end notched flexural (ENF) specimen is used. The ENF fracture specimen is essentially a three point flexure specimen with an embedded through width delamination placed at laminate mid surface. It is shown by Carlsson et al.(1986), that ENF specimen has been found to produce shear loading at the crack tip without excessive friction between crack surfaces.

The ENF specimen is shown in Fig 5.1. Both ENF and DCB specimen were cut from same plate. The method of DCB specimen fabrication as given in Sec.4.3.1 is also followed for preparing ENF specimen.

### **5.2.2 Experimental Procedure**

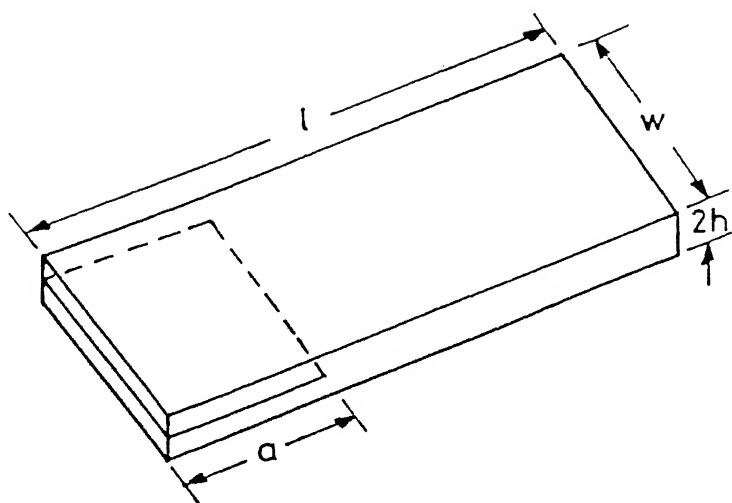
The specimen was subjected to three point bending on a properly aligned and calibrated Instron testing machine. The specimen loading set up is shown in Fig 5.2.a The test was carried on in displacement control mode. A cross head speed of 1 mm/min was used. The load cell was 100 kN (maximum capacity) and load range set was 5 kN. A real time plot of the load vs. displacement was made on an x-Y recorder. Only one loading cycle can be performed for each specimen since the crack growth is unstable. A photograph of mode II test set up is given in Fig.5.2.b.

### 5.2.3 Data Reduction

The present data reduction scheme is based on elastic beam theory expression for compliance and strain energy release rate of ENF specimen. From elastic beam theory, an expression for strain energy release rate can be derived as( Russell et al. 1985)and Carlsson et al. 1986)

$$G_{II} = \frac{9p^2Ca^2}{2b(2l^3+3a^3)} \quad (5.1)$$

where P is the applied load, C is the compliance, a is the crack length, b is the width of specimen and l is span between central loading and outer support. In the present work, the compliance is determined from the slope of load vs displacement curve.



$l = 112 \text{ mm}$   
 $w = 26.5 \text{ mm}$   
 $2h = \simeq 3 \text{ mm}$   
 $a \simeq 30 \text{ mm}$

Fig.5.1 Geometry of ENF specimen.

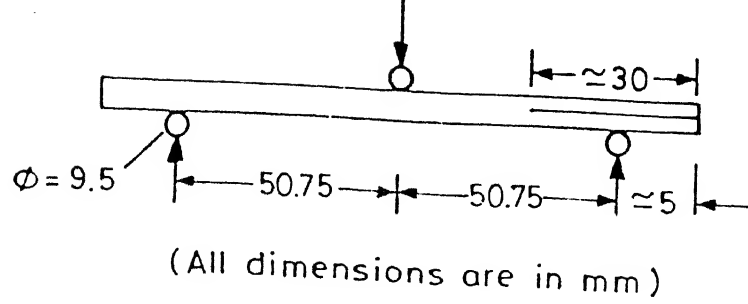


Fig.5.2.a ENF loading of the specimen in mode II.

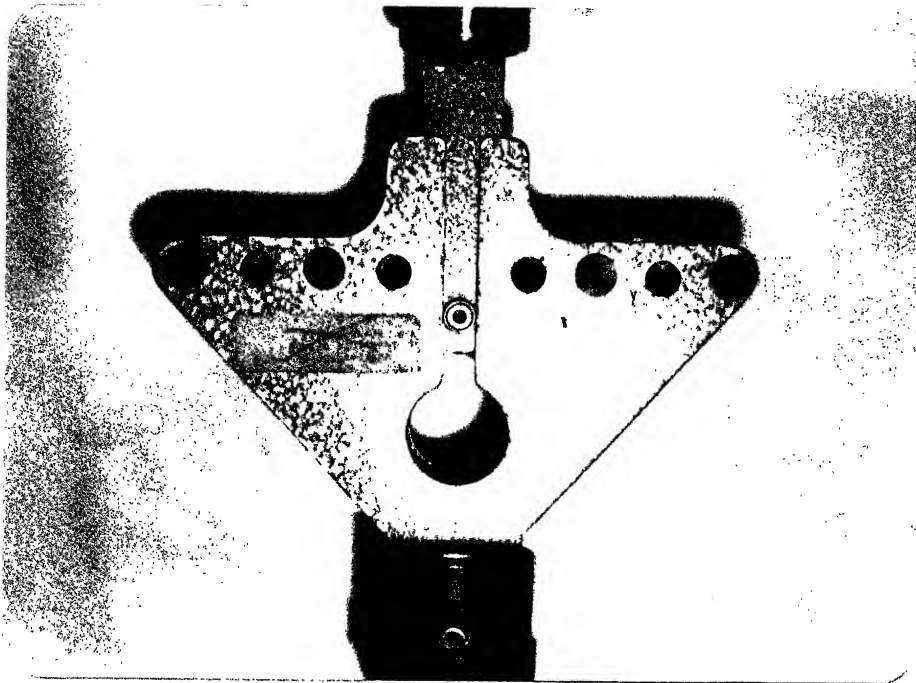


Fig.5.2.b Photograph of experimental set up of mode II test.

### 5.3 RESULT AND DISCUSSION

Both chemically modified and unmodified specimens of dimension given in Sec.5.2.1 are tested in mode II as describe in Sec.5.2.2. The typical load vs. deflection curve obtained in testing is given in Fig 5.3 for both types of laminates. From the above figure it is obvious that more load required in the case of modified laminate than of unmodified laminate for same deflection of specimens. The critical loads for crack initiation is also higher for modified laminate than unmodified laminate. This approves that crack initiation resistance of modified laminate is more.

The experimentally determined values of interlaminar  $G_{IIc}$  of both chemically unmodified and modified specimens are given in Table 5.1 and Table 5.2. respectively. The average value of their  $G_{IIc}$  has also been given in the respective tables. From the  $G_{IIc}$  value presented in the tables, it can be deduced that  $G_{IIc}$  of rubber modified specimen is 47% more than corresponding  $G_{IIc}$  of unmodified specimens. Thus from above results it can be concluded that mode II delamination resistance of modified laminates also contribute towards the improvement of impact induced damage of modified laminate over unmodified laminates.

The improvement in the  $G_{IIc}$  of modified laminate can be attributed to presence of large rubber particles in the matrix of laminate. These large rubber(CTBN) particles changes the local dialational deformation to shear deformation. Thus large scale shearing and plastic deformation are the main mechanisms responsible for chemically modified

laminate  $G_{IIC}$  improvement.

Laminates fabricated with chemical treatment of epoxy by CTBN showed reduction in the impact induced area by 60%, increase of  $G_{Ic}$  by 40% and increase of  $G_{IIC}$  by 47%. It is thus worthnoting that reduction in impact induced area is almost same as the increase in interlaminar  $G_{Ic}$  and  $G_{IIC}$ .

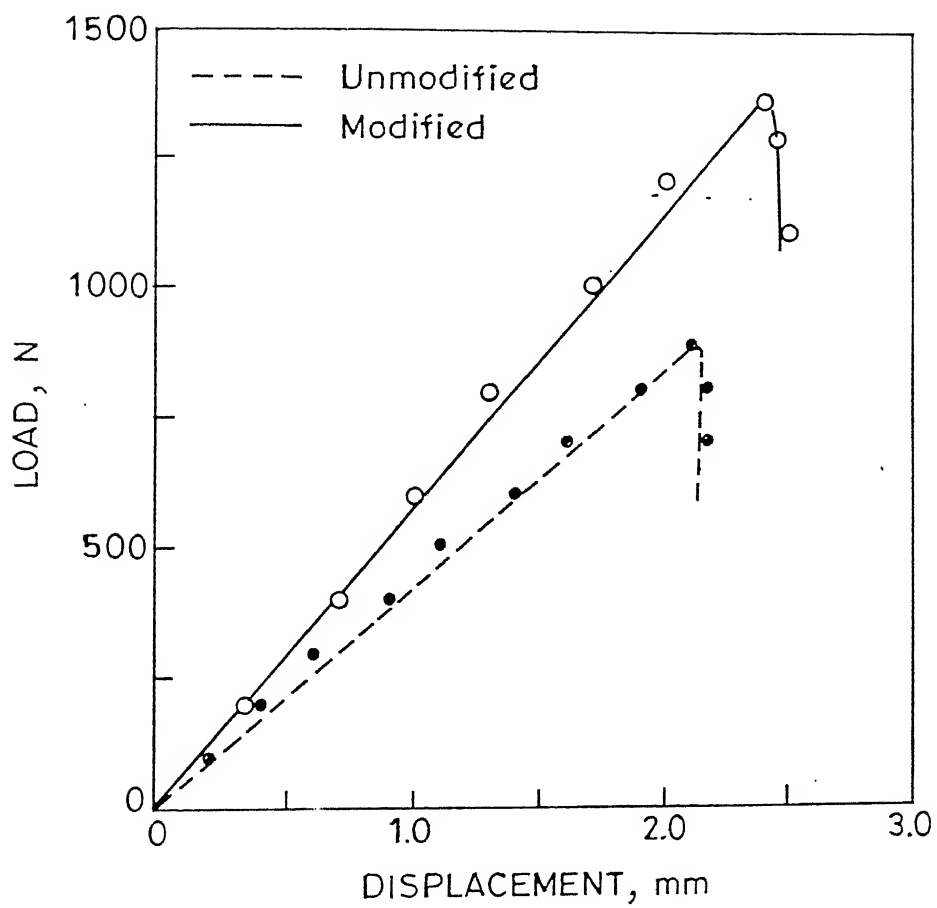


Fig.5.3 A typical load vs. displacement curve of mode II test.

**Table 5.1 Interlaminar  $G_{IIC}$  of chemically unmodified laminates**

Specimen number	Interlaminar $G_{IIC}$ (J/m <sup>2</sup> )	Average interlaminar $G_{IIC}$ (J/m <sup>2</sup> )
G2U-1	990	923
G2U-2	1021	
G2U-3	769	
G2U-4	913	



**Table 5.2** interlaminar  $G_{IIC}$  of chemically modified laminates

Specimen number	Interlaminar $G_{IIC}$ (J/m <sup>2</sup> )	Average interlaminar $G_{IIC}$ (J/m <sup>2</sup> )
G2M-1	1490	1359
G2M-2	1040	
G2M-4	1383	
G2M-4	1531	
G2M-5	960	
G2M-5	1169	
G2M-7	1667	
G2M-9	1633	

# TENSILE TESTING

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### 6.1 INTRODUCTION

Tensile strength and modulus are the basic properties of a material by which a preliminary at-sight-judgement is done to material. Only because of its higher specific tensile strength, composite materials are replacing other materials.

In the past there are many reports for enhancement of fracture toughness. But most of the developments were at the cost of strength of composite materials. Therefore, the concern of this work is to see whether tensile strength and modulus deteriorate or improve while trying to increase interlaminar toughness.

For this purpose, tensile specimens of both modified and unmodified laminate are prepared with the dimension as shown in Fig. 6.1. The testing of both type specimens is performed on MTS machine. These values of ultimate tensile strength and modulus will reflect the effect matrix modification has on tensile properties.

## **6.2 EXPERIMENT TECHNIQUE**

### **6.2.1 Specimen**

The geometry of specimen and tabs with their dimensions are shown in Fig.6.1. The Laminate for tensile specimens is prepared in the way as discussed in Sec.2.8. Following the specification of ASTM code, the laminate's edges are smoothened on water-proof emery paper till the dimensions of the specimen are achieved. This eliminates undercut or notches at the edges of the specimen. The end tabs also made of glass fibre/epoxy laminates were bonded to the sides as shown in Fig.6.1. The adhesive used for bonding was same as employed for making the specimen laminate. Tabs of proper length were made to avoid shear failure of tabs during experiment.

### **6.2.2 Experiment Procedure**

The tensile test is conducted as per ASTM D30.39.76 (revised 1982). For experiment, the specimen is loaded in a MTS (Material testing systems) machine of 10 ton capacity. The alignment of the two grips are checked before loading the specimen. The load is applied at a rate of 1 mm per minute in the longitudinal direction in tensile mode. The specimen is kept loaded until failure. A real time load vs displacement curve is obtained in the experiment.

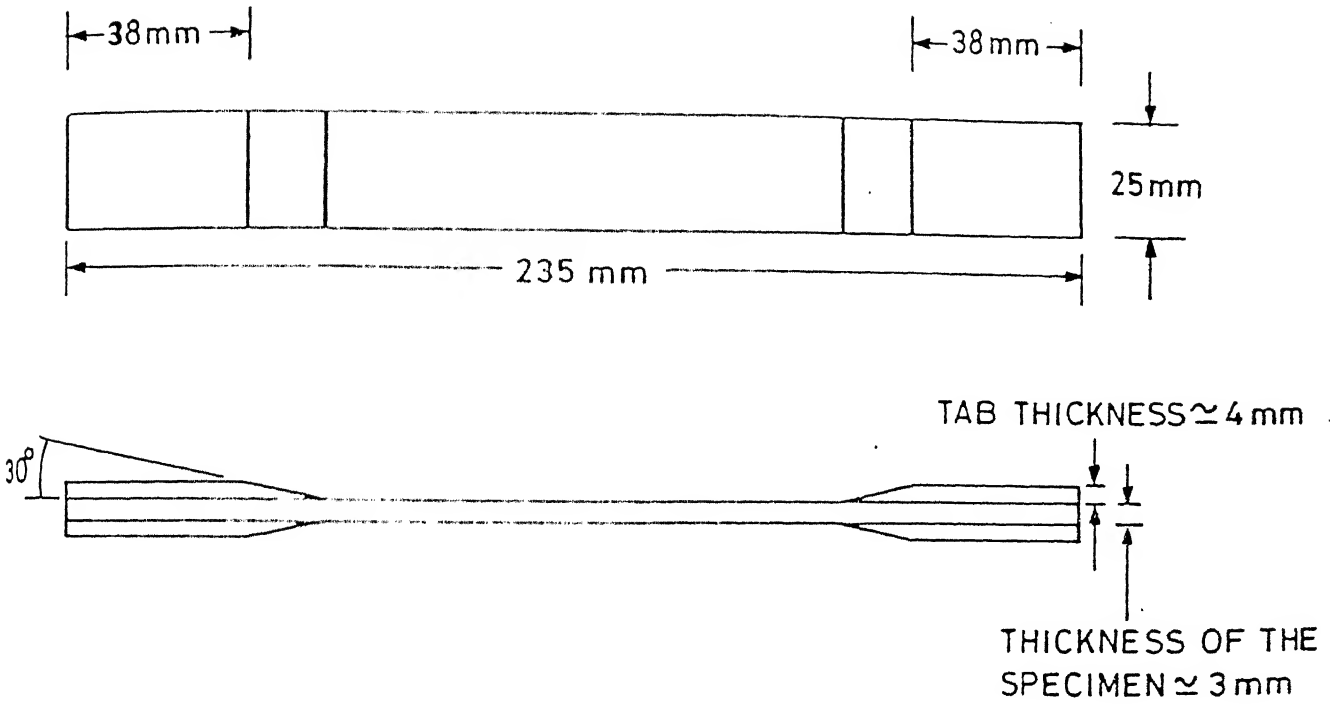


Fig.6.1 Tensile test specimen.

### **6.3 RESULT AND DISCUSSION**

Both modified and unmodified specimen are tested by the same method. A typical load vs. displacement curve for both laminates obtained tensile testing is shown in Fig.6.2. The values of ultimate tensile strength and modulus of unmodified laminates are given in Table 6.1 and for the chemically modified laminates are given in the Table 6.2. The chemically modified laminates shows marginally (8.2 % ) deterioration in the value of modulus as compare to unmodified laminates. While the ultimate strength of modified laminates shows marginally (10.8 %) improvement over unmodified laminates. This reduction in modulus of modified laminate is due to plasticizing effect of rubber particles in the rubber/epoxy solution.

### **6.4 CLOSURE**

Strength and modulus of modified laminates are only marginally altered and therefore tensile properties are not a concern of chemical modification of epoxy with CTBN.

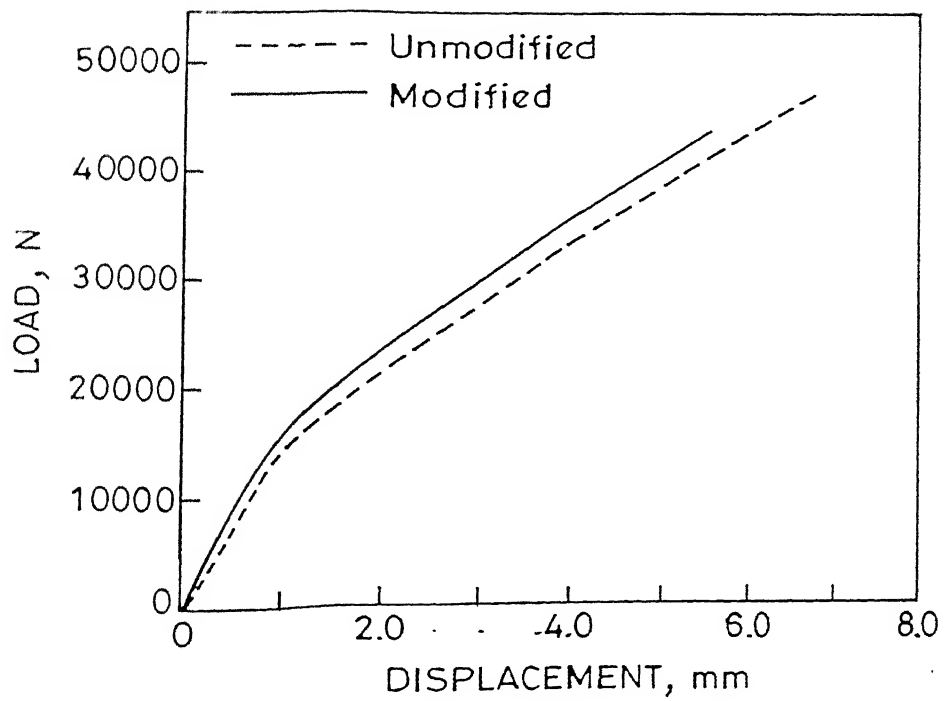


Fig.6.3 A typical load vs. displacement curve of tensile test.

**Table 6.1 Ultimate tensile strength and modulus of chemically unmodified laminates**

Specimen number	Ultimate tensile strength	Modulus	Average ultimate tensile strength	Average modulus
	Mpa	Gpa	Mpa	GPa
TU-1	258	20.9	286	20
TU-2	292	21.1		
TU-3	299	19.9		
TU-4	296	18.2		

**Table 6.2 Ultimate tensile strength and modulus of chemically modified laminates**

specimen number	ultimate tensile strength	modulus	avearge tensile strength	average modulus
	Mpa	Gpa	Mpa	Gpa
TM-1	316	19.1	317	18.5
TM-2	320	18.8		
TM-3	315	17.9		
TM-4	317	18.2		



### SUMMARY OF RESULTS AND CONCLUSION

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#### 7.1 SUMMARY

This work was undertaken to improve the impact damage area tolerance of polymer composite laminates through chemical treatment of laminate matrix material. The matrix material has been modified with CTBN 1300X8 and triphenylphosphine at inert nitrogen gas atmosphere in a special design gas chamber.

The response of chemically modified and unmodified laminates to the characteristics studied are summarised in Tab. 7.1. The chemical treatment has improved the impact damage area of laminate remarkably. To know the mechanisms responsible for impact damage area improvement of modified laminate over unmodified laminate, the mode I and mode II interlaminar toughesses have also been determined experimentally for both type of laminates. Both mode I and mode II interlaminar toughness have shown

significant improvement. The effect of chemical treatment on tensile properties of laminate is also investigated. The tensile strength and modulus of laminate do not show any significant change due to chemical treatment.

The impact damager area tolerance improvement of polymer composite laminate which was the main aim of present work has been successfully achieved without any loss of tensile properties of modified laminate.

## **7.2 SUGGESTION FOR FUTURE WORK**

- (1) Other properties of modified laminates such as environmental degradation, shear strength and modulus should be tested and compared with those of unmodified laminates.
- (2) The work should be repeated on CFRP laminates because of their much higher demand in aerospace applications.

**Table 7.1 Summary of The Experimental Investigation**

Characteristic	Chemically unmodified laminate	Chemically modified laminate	% of change	Comment
Impact Induced Damage area (cm <sup>2</sup> )	13	6.5	- 60	Significant Decrease
Interlaminar Fracture Toughness in Mode I (J/m <sup>2</sup> )	339	477	40	Significant increase
Interlaminar Fracture Toughness in Mode II (J/m <sup>2</sup> )	923	1359	47	Significant increase
Tensile Strength (MPa)	286	317	10.8	No Significant change
Modulus (GPa)	20	18.5	- 7.5	No significant change

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